PROTECTIVE COATINGS FOR METALS

BY

R. M. BURNS, Ph. D.
ASSISTANT CHEMICAL DIRECTOR
BELL TELEPHONE LABORATORIES

AND

A. E. SCHUH, Ph. D.
DIRECTOR OF RESEARCH
UNITED STATES PIPE AND FOUNDRY COMPANY

American Chemical Society
Monograph Series

BOOK DEPARTMENT
REINHOLD PUBLISHING CORPORATION
330 WEST FORTY-SECOND STREET, NEW YORK, U. S. A.

1939

3169

540.0202
N31 79

Copyright, 1939, by
Reinhold Publishing Corporation
All Rights Reserved

INDIAN INSTITUTE OF SCIENCE
LIBRARY
BANGALORE

PRINTED IN THE UNITED STATES OF AMERICA
INTERNATIONAL TEXTBOOK PRESS, SCRANTON, PA.

GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, secretary of the society, Washington, D. C.; the late John E. Teeple, then treasurer of the society, New York; and Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the A. C. S. series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successors) of New York.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed editors (the present list of whom appears at the close of this introduction) to have charge of securing authors, and of considering critically the manuscripts submitted. The editors endeavor to select topics of current interest, and authors recognized as authorities in their respective fields.

The development of knowledge in all branches of science, especially in chemistry, has been so rapid during the last fifty years, and the fields covered by this development so varied that it is difficult for any individual to keep in touch with progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and by such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin Kraut's Handbuch der Anorganischen Chemie, Moissan's Traité de Chimie Minérale Générale, Friend's and Mellor's Textbooks of Inorganic Chemistry and Heilbron's Dictionary of Organic Compounds, it often takes a great deal of time to coördinate the knowledge on a given topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value. It was with a clear recognition of the usefulness of such work that the American Chemical Society undertook to sponsor the publication of the two series of monographs.

Two distinct purposes are served by these monographs: the first, whose fulfillment probably renders to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a form intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs enable such men to form closer contact with work in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made, and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, extended references to the literature enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection is made of those papers which are most important.

AMERICAN CHEMICAL SOCIETY
BOARD OF EDITORS

Scientific Series:—
William A. Noyes, *Editor*,
S. C. Lind,
W. Mansfield Clark,
Linus C. Pauling,
L. F. Fieser.

Technologic Series:
Harrison E. Howe, *Editor*,
Walter A. Schmidt,
F. A. Lidbury,
E. R. Weidlein,
C. E. K. Mees,
F. W. Willard,
Carl S. Miner,
W. G. Whitman,
C. H. Mathewson,
Thomas H. Chilton.

Preface

In 1927 H. S. Rawdon's *Protective Metallic Coatings* appeared in the present monograph series. When, about three years ago, it became time to revise the work, Mr. Rawdon felt himself unable to undertake the task. The present authors were then invited, with Mr. Rawdon's kind consent, to prepare the revision. After a survey of the field it was concluded that the scope should be enlarged to include protective coatings of all types, including paints. It was felt that in this way the reader interested in corrosion prevention might be given more comprehensive information on the subject.

It was expected originally that the present treatise would consist essentially in a revision of Mr. Rawdon's earlier work enlarged in scope. Owing to the great technological advances of the past decade and the thousands of papers which have appeared in the protective coating field it soon became evident that a new treatise was desirable.

The present volume is designed primarily for those who have problems of protection; it is not intended to be a manual for the production of protective coatings although considerable information is given on this phase of the subject so that the reader may have a better understanding of the nature of the various coatings. As far as practicable, patented coatings and methods are so indicated in the references; but the absence of patent reference does not necessarily imply that a means or method is in the public domain. Neither should it be assumed that the mention of any patented or proprietary coating is in any sense a recommendation for the application or use of such coating.

Chapters 13, 14 and 15 were written by Mr. Schuh, who was at the time a member of the technical staff of Bell Telephone Laboratories. The other chapters have been prepared by the senior author. In a number of chapters and particularly in Chapter 4, having to do with hot dipped coatings, it has been possible to utilize considerable material from Mr. Rawdon's monograph; also a number of the illustrations in that work have been reproduced.

The authors are greatly indebted for critically reading portions of the manuscript and for helpful advice to: C. W. Borgmann, formerly of the National Tube Co. but now of the University of Colorado, W. H. Finkeldey of Singmaster and Breyer, G. O. Hiers of the National Lead Co., W. W. Higgins of the A. O. Smith Co., R. J. McKay and W. A. Wesley of the International Nickel Co., D. J. Macnaughton, T. P. Hoar, and W. E. Hoare of International Tin Research and Development Council, London, R. B. Mears of the Aluminum Company of America, E. E. Poste of Chattanooga, Tenn., L. R. Schlundt of Republic Lead Equipment Co., W. Blum, T. A. Denison, K. H. Logan, S. P. Ewing and E. F. Hickson of the National

Bureau of Standards, M. Brown of the Western Electric Co., and H. G. Arlt, W. E. Campbell, K. G. Compton, C. D. Hocker and C. H. Sample, their colleagues in Bell Laboratories.

Particular thanks are due to H. E. Haring, who critically read the entire manuscript and collaborated in the preparation of Chapter I.

Finally, the authors take pleasure in expressing their appreciation to R. R. Williams, Chemical Director of the Bell Telephone Laboratories, for his encouragement and advice.

R. M. BURNS

New York, N. Y.
November 15, 1938

Foreword

The advances which have been made in the metal-coating industry during the past decade have been so numerous and important that one is inclined to speak in superlatives in referring to them. In the class of metallic coatings, these advances have been especially striking in the field of electroplating. Not only have plating methods been extended and applied on a mass production scale, as in the zinc coating of wire and the tin plating of continuous steel strip, but entirely new processes, such as "bright plating," have been developed. The commercial application of these with the attendant saving in labor has been of great importance. The perfecting of the anodic oxidation process for aluminum has assisted greatly in successfully establishing the position of this metal as an engineering structural material and much the same can be said of magnesium. Improvements in older methods of coating, though not so spectacular, have been just as important industrially, as is evidenced by the exceedingly widespread use of the phosphate treatment for sheet steel in automobile bodies and other shapes prior to the application of the finishing coat. The success attained in the development of new and improved finishes of an organic nature is familiar to every user of metal products.

The body of information on protective coatings for metals resulting from the investigations on this subject in the years which have elapsed since the appearance of the previous monograph on the subject is so great that when the subject of revision arose, the preparation of an entirely new book appeared to be the most desirable course to follow. The need for information on coatings of a nonmetallic nature which are now so widely used in competition with or interchangeably with metallic coatings prompted the extension of the scope of the monograph to include paints and other applied organic coatings.

The active interest manifested during the past few years in investigations on the general subject of the corrosion of metals has led to the carrying-out of long-time exposure tests which yielded much new basic information having a direct bearing on our knowledge of the useful life of coatings and coated metals. The authors have wisely incorporated a great deal of this information in the discussion of the different types of coatings. Likewise, it has been deemed desirable to devote considerable space to the preliminary preparation of metal surfaces before the application of the coating since the quality of any coating is so dependent upon this factor.

The new monograph, therefore, covers a much broader field than did the previous one which was really a pioneer in the field of metallic coatings.

The investigator of the abstruse problems of corrosion as well as the materials engineer seeking practical help in combating this problem by preventing corrosion by protecting the surface will find this volume a veritable mine of information on all phases of the subject.

December 8, 1938 H. S. RAWDON
National Bureau of Standards
Washington, D. C.

INDIAN INSTITUTE OF SCIENCE
LIBRARY
BANGALORE

Table of Contents

PAGE

CHAPTER 1. PROTECTIVE COATINGS AND THE MECHANISM OF CORROSION....... 13

CHAPTER 2. SURFACE PREPARATION FOR THE APPLICATION OF COATINGS........ 30

CHAPTER 3. TYPES OF METALLIC COATINGS AND METHODS OF APPLICATION..... 35

Historical. Immersion in Molten Metal—"Hot Dipping": Principles, General Nature of Hot-Dipped Coatings, Practical Aspects of Hot-Dipping Process, Extension of Hot-Dipping Process. Cementation: Mechanism of the Process, Character of the Coating, Practical Applications, Cemented or Sintered Carbide Coatings. Mechanically-formed Coatings—"Metal-Cladding." Electroplating: Principles, Character of Deposit. Metal Spraying and Sprayed Metal Coatings: Surface Preparation for Metal Spraying, The Nature of Sprayed-Metal Coatings, Practical Applications of Metal Spraying. Cathode Sputtering: Equipment and Method of Operation, Commercial Applications of Sputtered Coatings. Coatings by Condensation of Metal Vapor.

CHAPTER 4. ZINC COATING BY HOT-DIPPING PROCESS........................ 57

History of Zinc and the Hot-Dipping Process. Outline of the Hot-Dipping Process: Preparation of the Base Surface: Pickling Treatment for Removal of Scale, Fluxing Treatment, Other Methods of Surface Preparation. The Molten Metal Bath: Formation of Iron-Zinc Alloy or Dross, Effect of Metallic Additions to Zinc Bath, Other Factors which Affect Character of Zinc Coatings. The Microstructure of Iron-Zinc Alloys. Effect of Hot-Dipping Process on the Base Metal. Surface Appearance of Zinc-coated Sheets after Storage.

CHAPTER 5. ZINC COATING BY ELECTROPLATING AND CEMENTATION............ 76

Electroplating: Plating Baths, Anodes, Plating Tanks and Mechanical Equipment, Electroplating of Wire, Bright Zinc Electroplating, Properties and Structure of Electroplated Coatings. Zinc Coating by Cementation—"Sherardization": Outline of the Process, Effect of Temperature, Structure of Coating, Mechanism of Zinc Cementation Process.

CHAPTER 6. PROTECTIVE VALUE OF ZINC COATINGS........................... 90

Nature of Protective Action of Zinc Coatings. Performance of Zinc Coatings in the Atmosphere: Distinctive Properties of Various Types of Coatings, Comparative Life of Different Types of Zinc Finishes, Effect of Impurities upon Corrosion of Zinc Coatings in the Atmosphere, Influence of Environment on Life of Coatings, Conclusions Respecting Life of Zinc Coatings in Outdoor Atmosphere. Performance of Zinc Coatings in Indoor Atmospheres. Performance of Zinc Coatings in Submerged Exposures: Behavior of Zinc Coatings in Natural Waters, Corrosion of Zinc Coatings in Sea-Water and Chloride Solutions, Effect of Impurities upon Corrosion of Zinc in Acids, Protective Value of Zinc Coatings Against Corrosion Fatigue of Steel. Performance of Zinc Coatings in Soils. Toxic Properties of Zinc.

CHAPTER 7. CADMIUM COATINGS AND THEIR PROTECTIVE VALUE.............. 124

Method of Application of Cadmium Coatings. Protective Value of Cadmium Coatings.

PAGE

CHAPTER 8. TIN COATINGS 130

Hot-Dipped Tin Coatings: Historical, Outline of the Process, Hand Dipping, Mechanical Dipping, Operating Conditions of the Molten Tin Bath, Structure of Hot-Dipped Coatings, Tin-Plate Commercial Terms. Electroplated Tin Coatings: Tin-Plating Baths, Electroplating of Steel Strip. Tin Coatings by Immersion Process. Tinning of Copper. The Use of Tin Plate in the Canning Industry. Corrosion Resistance of Tin Coatings: Performance in the Atmosphere, Performance in Aqueous Solutions. Recovery of Tin from Tin-Plate Scrap.

CHAPTER 9. NICKEL AND CHROMIUM COATINGS 160

Nickel Coatings: Nickel Plating Solutions, Application of Nickel Plating to Aluminum and Zinc Alloys, Application of Heavy Electroplated Coatings, Bright Nickel Plating, Nickel-Clad Steel, Corrosion Resistance of Nickel Coatings. Chromium Coatings: Historical, Theory and Practice of Chromium Plating, Chromium Cementation—"Chromizing," The Performance of Chromium Plated Coatings.

CHAPTER 10. COATINGS OF COPPER, LEAD, ALUMINUM AND MISCELLANEOUS METALS 190

Copper Coatings: Electroplated Copper Coatings, Structure of Electroplated Copper Coatings, Adhesion of Electroplated Copper Coatings, Use of Electroplated Copper in Selective Carbonization of Steel, Mechanical Copper-Coating Process, Miscellaneous Copper-Coating Methods, Corrosion Resistance of Copper Coatings. Lead Coatings: The Hot Dipping Process, Lead Linings, Terne Plate, Electroplated Lead Coatings, The Corrosion Resistance of Lead Coatings. Aluminum Coatings: Hot Dipped Aluminum Coatings, Calorizing, Mechanically Applied Aluminum Coatings—"Alclad" Products, Corrosion Resistance of Aluminum Coatings. Miscellaneous Metallic Coatings: Brass Coatings, Cobalt Coatings, Tungsten Coatings, Tantalum Coatings.

CHAPTER 11. COATINGS OF NOBLE AND RARE METALS .... [illegible]

History of Gilding and Silvering of Metals. Electroplated Silver Coatings: Thickness of Silver Plating, Defects in Silver Coatings, Tarnishing of Silver. Gold Coatings. Rhodium Coatings. Platinum and Palladium Coatings. Indium Coatings. Rhenium Coatings.

CHAPTER 12. METHODS OF TESTING METALLIC COATINGS .... [illegible]

General. Determination of Quality of Metallic Coatings: Physical Tests: Bend Test for Sheets, Bend Test for Wire, Adhesion Tests. Tests for Average Thickness of Coating: Sampling of Zinc-Coated Sheet and Wire, Hydrochloric Acid-Antimony Chloride Method, Sulfuric Acid-Arsenious Oxide Method, Basic Lead Acetate Method, Other Chemical Stripping Methods, Electrolytic Methods, Hydrogen Evolution Method, Heat of Reaction Test, Chord Method, Magnetic Methods, Metallographic Examination of Coating. Tests for the Uniformity of Coating: Preece Test, Acetic Acid Hydrogen Peroxide Test, Sulfuric Acid Test, Dropping Test, Jet Test for Nickel and Other Coatings, Other Tests for Uniformity of Coating. Determination of Porosity: Ferroxyl Test, Hot-Water Test, Sodium Chloride Hydrogen Peroxide Test, Electrographic Methods, Other Porosity Tests. Determination of Rate of Corrosion: Atmospheric Corrosion Testing, Corrosion Testing in Liquids, Soil Corrosion Testing. Accelerated Corrosion Tests: Salt Spray Test, Intermittent Immersion Tests. Sensitive Methods for the Study of Corrosion Reactions: Microchemical Methods, Electrochemical Techniques.

CHAPTER 13. COMPOSITION OF PAINTS AND MECHANISM OF FILM FORMATION 275

Historical. Classification of Organic Finishing Materials: Paints, Enamels, Lacquer Enamels. Organic Finish Components: Film Formation, The

PAGE

Drying Oils, Linseed Oil, Perilla Oil, Tung Oil, Oiticica Oil, Soybean Oil, Fish Oils. Driers. Resins: Natural Resins, Synthetic Resins. Pigments and Pigmentation.

CHAPTER 14. THE DURABILITY AND EVALUATION OF PAINTS 298
Factors Determining Durability. Electrochemical Aspects. Pigments Used for Corrosion Protective Purposes: Red Lead, White Lead, Chromates, Iron Oxide, Zinc Pigments, Aluminum Powder, Carbon Pigments, Other Metallic Pigments. Evaluation of Priming Pigments. Adhesion: Initial Adhesion, Effect of Inorganic Contaminants. Permeability. Structural Properties of Organic Coatings: Poly-condensation Resins, Varnishes, Bituminous Materials. Evaluation of Durability: Exposure Testing, Results of Exposure Tests, Accelerated Exposure Tests, Evaluation by Physical Tests.

CHAPTER 15. PAINT PRACTICES 346
Painting of Exposed Steel Structures. Painting of Industrial Equipment. Protection of Underground Pipe.

CHAPTER 16. MISCELLANEOUS COATINGS 368
Electrolytic Oxide Coatings on Aluminum. Surface Conversion or Chemical Dip Coatings: Protective Films Induced by Presence of Alkalies and Oxidants, Preservation of Metals and Machinery by Slushing Compounds, Vitreous Enamel Coatings.

AUTHOR INDEX 387

SUBJECT INDEX 395

INDIAN INSTITUTE OF SCIENCE
LIBRARY
BANGALORE

INDIAN INSTITUTE OF SCIENCE
LIBRARY
BANGALORE

Chapter 1

Protective Coatings and the Mechanism of Corrosion

Many metals of industrial importance, notably iron and steel, require protection against corrosion. The character and extent of the necessary protective measures depend upon the nature of the metal, and of the environment to which the metal is exposed. There are a number of general methods for the preservation of metals. Where control of the environment is feasible, it may be possible to eliminate or minimize one or more of such corrosive factors as oxygen, humidity, dust and sulfurous gases. Among common examples of this method are deaeration of water in boilers and closed water systems,[1] and reduction of atmospheric pollution by means of air-conditioning apparatus. Measures of this kind are exceedingly effective in extending the useful life of metals and metallic products. All other methods of corrosion control seek to interpose a protective film between the metal and its surroundings, and it is with this subject that the present monograph is concerned.

Protective coatings may be formed naturally or synthetically, or by both methods. In reality, naturally formed protective coatings are corrosion products of a certain character which may be obtained by the introduction of the protective agent into the metal, as, for example, the use of chromium and nickel in alloy steels, or tin in Admiralty metal; or the films may be produced by purposely adding the protective constituent to the environment, as in the use of soluble chromates in recirculating water systems, automobile radiators, and air-conditioning equipment. The relatively good corrosion resistance of the common non-ferrous metals is due to the nature of the surface films which these metals develop in ordinary environments. In any case, these self-formed protective films are the result of the conversion of the metal surface into a chemical compound which is held to the surface by atomic forces. Such films are usually continuous, of low solubility, relatively impermeable, and often invisible. Noble metals may form protective films under some circumstances, but in general the relative incorrodibility of these metals as a class is due to their chemically unreactive character.

Synthetic protective coatings are of great variety. The two most common classes are metallic coatings, employing almost any non-ferrous metal except the alkali and alkaline earth metals, and organic coatings which may consist of paints, lacquers, enamels, oils, waxes or bitumins. Coatings of inorganic substances such as vitreous enamels, cement, concrete and clay products, while relatively less important, are coming into wider use for certain purposes. These three types of coating have their advantages and their limitations. The following chapters will describe in some detail what these coatings are, how they are obtained and evaluated, and how they perform. Before undertaking this project, however, it would seem appropriate to consider at some length the nature of corrosion processes and how these are affected by the presence of protective coatings.

---

[1] Speller, F. N., "Corrosion, Causes and Prevention," 2nd ed., p. 384, New York, McGraw-Hill Book Co., 1935.

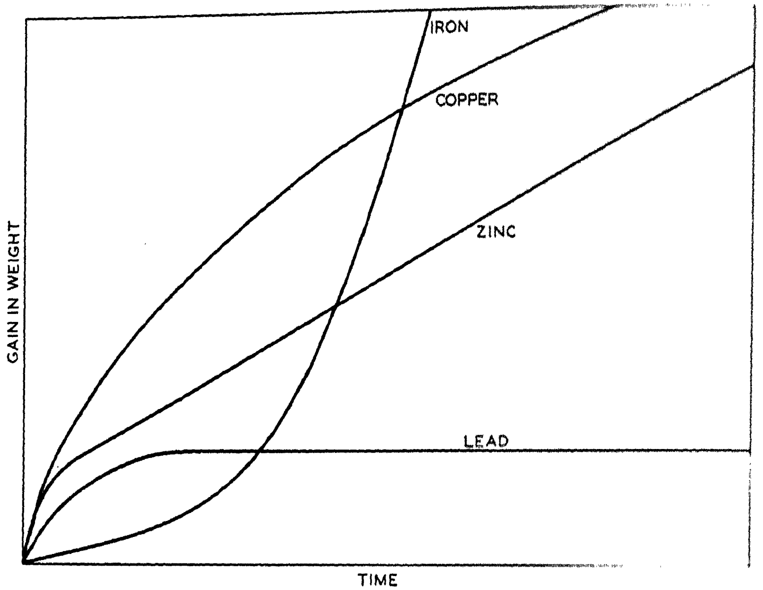


Figure 1.—Corrosion-Time Relationships of Certain Metals Exposed to the Atmosphere.

The metallic state is uncommon in nature. It is well recognized, as implied above, that metals corrode by means of chemical reactions with the non-metallic elements of their surroundings. The more heterogeneous the metal and the more complex the environment, the more complicated may be the process of corrosion. The composition, physical state and surface condition of the metallic material, as well as the chemical components of the surrounding medium—their phases and concentrations determine the nature of corrosion reactions. Other important variables affecting corrosion processes are the temperature, temperature fluctuation, movement or circulation of the medium in contact with the metal surface, the nature and solubility of the corrosion products, and particularly the position in which these products are precipitated with reference to the surface of the corroding metal. In spite of all these complexities it is generally possible, from an understanding of the mechanism of corrosion and from observations of corrosion behavior, to recognize the controlling variables in given instances of corrosion.

In this connection it is of interest to consider the film-forming characteristics of certain metals exposed to indoor summer atmosphere. Figure 1 gives the gain in weight with time for copper, zinc, lead and iron for such exposure.[2] Rain, relative humidity, atmospheric pollution, dust, and temperature and temperature fluctuation may all have a bearing upon the results obtained for individual metals in ordinary atmospheres. It will be observed that the relationship for copper is parabolic in type, indicating that the process is controlled by the rate of diffusion of oxygen or other reactants through an increasingly thicker surface film, presumably of oxide. Silver is known to display a similar characteristic, even at very high humidities, and the film consists of silver sulfide. Thin films formed on copper in pure air are impervious to volatile sulfur compounds but oxide films produced on silver appear to be converted to sulfide by subsequent exposure to air containing sulfurous gases. The curve shown for zinc, which may be obtained for iron also under certain circumstances,[3] is in harmony with the view[3a] that the oxide first formed is pseudomorphic with the underlying metal, and that upon attaining a certain thickness the film becomes granular in character and does not further influence the rate of corrosion. The corrosion-time curve for lead becomes parallel with the time axis after the initial stages. The film in this case becomes impervious to the constituents of the environment and is the so-called "self-healing" type, of which the air-formed film on aluminum is another example.

The curve shown for iron in Figure 1, which may be obtained also for nickel, copper, zinc and many other metals at high humidities, indicates that the film which forms in the initial stages of the exposure exerts an accelerating influence upon the subsequent rate of corrosion. Iron displays a markedly lower "critical" humidity which falls within the range 40 to 65 per cent relative humidity, and this humidity range probably obtained in the case under consideration. By the term critical humidity is meant the relative humidity corresponding to the vapor pressure of a saturated solution of the corrosion products, and this depends upon the composition and to some extent the structure of these products. In other words the acceleration of corrosion is due in such cases to the water taken up by the corrosion products. The nature of the films which form on iron in the atmosphere at ordinary and elevated temperatures has lately been studied extensively by a number of investigators.[4] Curves of almost all the

[2] Adapted from Vernon, W. H. J., *Trans. Faraday Soc.*, **19**, 839 (1924); **23**, 113 (1927).

[3] Vernon, W. H. J., *Trans. Faraday Soc.*, **31**, 1668 (1935).

[3a] Finch, G. I., and Quarrell, A. G., *Proc. Phy. Soc.*, **46**, 148 (1934).

[4] See reference 3 and also Miley, H. A., and Evans, U. R., *J. Chem. Soc. (London)*, 1295 (1937); Miley, H. A., *Metallurgist*, Supplement to *Engineer*, **11**, April 30, June 25 (1937).

characteristics illustrated in Figure 1 may be had under the appropriate circumstances. It would appear that there are at least two forms of ferric oxide, one of which (α-Fe_2O_3) is stable above 200° C. and protective in character, and the other (γ-Fe_2O_3) stable below that temperature and more open and non-protective in structure. Very likely the films formed under ordinary atmospheric conditions are more or less hydrated.

Corrosion is a degradation process and is therefore characterized by the dissipation of energy in some form. The best measure of the tendency of a metal to corrode is, in thermodynamical terms, the decrease in free energy accompanying the reaction, *i.e.,* the difference in energy between the initial and final states of the system. This may be obtained by simple calculation and is of value in showing whether or not it is possible for corrosion to occur under the conditions defined.[5] There is no assurance, however, that reactions which are possible will actually take place within a reasonable time, if indeed at all. Once it is determined by calculation that a metal may corrode in a given environment, the problem becomes one of determining the rate of the reaction. Since this rate bears no direct relationship to the energy changes which are involved it cannot be predicted, but must be measured in some fashion.[6]

There are two general classes of corrosion reactions: those in which there is a direct combination of metal and non-metallic elements, and those in which the metal replaces hydrogen (or another metal) in compounds. The former is exemplified by oxidation, halogenation or sulfurization reactions, usually more evident at somewhat elevated temperatures or low humidities. The kinetics of individual reactions may be complex and often obscure. The second class of reactions usually involves replacement, by the corroding metal, of hydrogen from water or acids; this is well known to be an electrolytic process. Recent theoretical studies have indicated that reactions of the first class may be also electrolytic in character.[6a] When metals corrode in the atmosphere either or both of these mechanisms may be involved depending upon circumstances. However, the practical problem of corrosion is chiefly concerned with replacement type reactions which occur in the presence of moisture. In view of this fact it seems desirable to examine the mechanism of this type of corrosion reaction in some detail.

It has been well established that, in the corrosion of a metal in aqueous environment, two reactions take place simultaneously upon its surface; metal ions pass into solution and hydrogen ions pass out of solution to form hydrogen gas, or combine with atmospheric oxygen to form water.* However, inasmuch as ions are matter and have dimensions, it is evident that both reactions cannot take place at the same point and that there must be two kinds of areas, those at which metal dissolves, and those at which hydrogen ions are discharged or consumed by oxygen. In postulating such a situation it is necessary to assume that the interface between a metal and its environment is not entirely homogeneous; otherwise there would be no basis for the selection and establishment of those two kinds of areas. There are in other words two types of interface between metal and environment at which different corrosion tendencies must exist. The known resistance of spectroscopically pure metals to solution even in acid is the result of the homogeneity of the metal-acid interface and not of a lesser tendency of the metals to dissolve. Unless specially prepared, metal surfaces contain areas which are chemically or physically different from the rest of the surface. The presence of metallic impurities, oxides, and differences in crystal structure and physical strain, which in turn lead to differences in solution tendencies, cannot readily be avoided. In actual practice, therefore, it is safe to assume that perfectly homogeneous metals are not commercially available; and even if they were, the chances of their environments being equally homogeneous are rather remote.

---

[5] Forrest, H. O., Roetheli, B. E., and Brown, R. H., *Ind. Eng. Chem.*, 23, 650 (1931).

[6] Johnston, J., *Ind. Eng. Chem.*, 26, 1238 (1934).

[6a] Wagner, C., *Z. Phys. Chem., B*, 21, 25 (1933); Hoar, T. P. and Price, L. E., *Trans. Faraday Soc.*, 34, 867 (1938).

* In neutral solution it is likely that the last-mentioned reaction consists merely in the formation of oxygen (or hydroxyl ions).

These areas of different solution tendency can be shown experimentally to have different electrolytic potentials. In the "galvanic cells" so formed, the areas which favor metal dissolution are the anodes, and those which favor hydrogen-ion discharge (or hydroxyl-ion formation from oxygen) are the cathodes.* The quantity of current which passes through these cells is proportional to the amount of metal which dissolves. This "couple" action provides the mechanism by means of which corrosion takes place.

The basis of any electrochemical treatment of the subject of corrosion is, of necessity, the "electromotive force series," an arrangement of the elements in the order of their dissolution tendencies. The position of some of the more common metals (and non-metals) in this series is shown below. The values of potential given are those calculated for the elements in solutions containing *in effect* one atomic weight in grams of ions in 1000 grams of water at 25° C.† For gas electrodes the gas pressure is assumed to be one atmosphere.

These standard potentials may be considered as the voltage of electrolytic cells in which one pole is the hydrogen electrode, designated arbitrarily as zero, and the other is the electrode in question. The sign of the electrode indicates its polarity in such a cell.

---

* Expressed in terms of electron transfer, the anodes are areas which tend to gain (or accept) electrons by the formation of positively charged ions (cations) or the discharge of negatively charged ions (anions); conversely the cathodes are areas which tend to lose electrons by the discharge of cations or the formation of anions.

† Actually more than one atomic weight in grams of a metal is required to obtain the theoretical ionic activity of one gram atomic weight in 1000 grams of water. For this reason the term "in effect" is employed and will later be implied when mention is made of ionic concentration. Solutions involved in most corrosion problems are so dilute that the actual and effective concentrations are of similar magnitude.

The fact cannot be too strongly emphasized that the relative position of any one of the metals (or non-metals) in the series is dependent not only upon its inherent solution or corrosion tendency, but also upon the effective concentration of ions of that metal which exists in the environment. It is well known that for every tenfold increase in the ionic concentration of a metal in its environment, the tendency for that metal to dissolve or corrode is decreased, that is, it becomes more electropositive by $\frac{0.059}{n}$ volt at 25° C., where n is the number of unit electrical charges on the ion, or in other words, the valence of the metal. The potential of non metals varies with concentration in like manner, with the difference that in this case an increase in ionic concentration causes the electrode to become more electronegative. The significance of the concentration factor in determining the position of a metal in the e.m.f. series is well illustrated by the fact that the positions of two metals so far apart as zinc and copper can be reversed, *e.g.,* in zinc cyanide solution. Under such circumstances, copper dissolves or corrodes more readily than zinc and actually displaces zinc from solution.

Another fact which must be taken into consideration in utilizing the e.m.f. series is that the gas electrodes, such as the hydrogen and oxygen electrodes included therein are assumed to be *at atmospheric pressure.* The concentration of gas in an electrode is equally as important in the establishment of a potential as the concentration of the corresponding ions in solution on the other side of the interface. For every tenfold decrease in hydrogen gas pressure, the potential of a hydrogen electrode becomes more electropositive by 0.029 volt. Conversely, for every tenfold decrease in oxygen pressure, the potential of an oxygen electrode becomes less electropositive by 0.015 volt.

As has been previously mentioned, the potentials of the electrodes listed in Table 1 are based on the assumption that the gas electrodes are at

Table 1.—The Electromotive Force Series (25° C.)

Electrode	Reaction	Potential (volts)
Gold	$Au, \rightarrow Au^{+++}$	+1.50
Chlorine	$\frac{1}{2}Cl_2, \rightarrow Cl^-$	+1.358
Silver	$Ag, \rightarrow Ag^+$	+0.798
Oxygen	$\frac{1}{2}O_2, \rightarrow OH^-$	+0.400
Copper	$Cu, \rightarrow Cu^{++}$	+0.344
Hydrogen	$\frac{1}{2}H_2, \rightarrow H^+$	±0.0000
Lead	$Pb, \rightarrow Pb^{++}$	0.12
Tin	$Sn, \rightarrow Sn^{++}$	−0.14
Nickel	$Ni, \rightarrow Ni^{++}$	−0.231
Cadmium	$Cd, \rightarrow Cd^{++}$	−0.401
Iron	$Fe, \rightarrow Fe^{++}$	−0.441
Zinc	$Zn, \rightarrow Zn^{++}$	−0.762
Aluminum	$Al, \rightarrow Al^{+++}$	−1.69

atmospheric pressure, and that the environment in all cases contains in effect one atomic weight in grams of ions of the element involved in 1000 grams of water. In this form the e.m.f. series is of little value in corrosion studies. To be useful it must be modified to meet the conditions of each individual problem. For example, let it be assumed that pure water is the corrosive environment. Pure water is known to be one-ten millionth normal * in hydrogen ions and to contain an equal concentration of hydroxyl (OH) ions. Since the concentration of each of these ions in water is seven tenfold changes from normal, the potential of the hydrogen electrode (at atmospheric pressure) in water is not zero as in Table 1 but 7×0.059 volt or 0.413 volt more electronegative (more anodic) than zero. In like manner, it can be calculated that the potential of the oxygen electrode at atmospheric pressure in water is not +0.400 volt, but +0.400 volt plus 7×0.059 volt, or +0.813 volt. The difference in potential between the hydrogen and oxygen electrodes (at atmospheric pressure) in water is therefore the difference between −0.413 and +0.813 volt, or 1.23 volts. This figure is a very convenient one to remember because, as can readily be calculated, it is a constant which is unaffected by the presence of dissolved salts, acids or alkalies. In other words, the difference in potential between the hydrogen and oxygen electrodes (at atmospheric pressure) in any aqueous environment is invariably 1.23 volts. (This theoretical value of 1.23 volts is never attained in practice owing to irreversible processes at the oxygen electrode.) For example, if sufficient acid were added to pure water to change it from pH 7 to pH 6, a tenfold increase in hydrogen ions and a tenfold decrease in hydroxyl (OH) ions would occur, and the potential of the hydrogen electrode would change from −0.413 volt to 0.354 volt, and the potential of the oxygen electrode from +0.813 volt to +0.872 volt. Thus the electrode potentials would be shifted simultaneously in the same direction and would still remain 1.23 volts apart.

The relationships which exist between the potentials of hydrogen and oxygen electrodes at any pressure up to atmospheric in environments ranging in acidity from normal in hydrogen ions (pH 0) to normal in hydroxyl ions (pH 14) are given in Figure. 2.[7] It will be noted that the reference zero of the potential scale in this diagram is identical with that employed in Table 1.

An atmospheric pressure hydrogen electrode can be established by bubbling hydrogen gas over a relatively inert or noble metal, such as platinum, which hydrogen readily permeates, or by impressing upon it just sufficient voltage to discharge hydrogen in the form of gas bubbles. Oxygen electrodes can be formed in an analogous manner with oxygen. In the corrosion process hydrogen electrodes are established on the

---

* That is, in effect one atomic weight in grams of hydrogen ions per liter of solution. For practical purposes this does not differ significantly from one atomic weight in grams of hydrogen ions in 1000 grams of water.

[7] Adapted from Clark, W. M., "Determination of Hydrogen Ions," 3rd ed., p. 387, Baltimore, Williams and Wilkins Co., 1928.

cathodic areas of the corroding metal by electrolytic action. The effective pressures of the hydrogen electrodes so formed may vary from almost zero to one atmosphere and even more, depending upon the relative rates of hydrogen discharge and hydrogen removal at the cathode surface. The

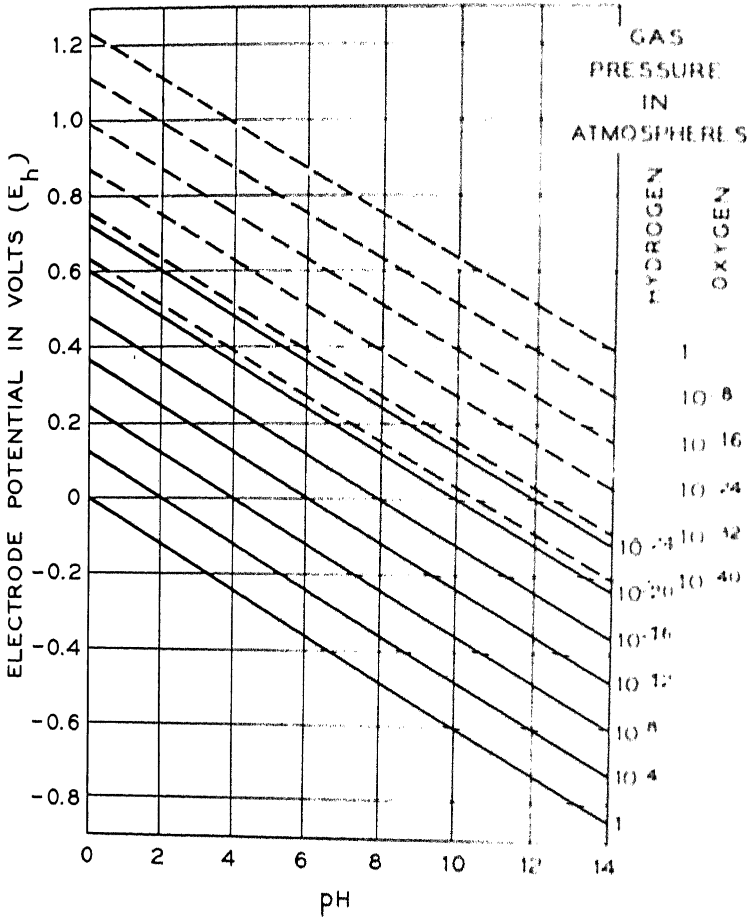


Figure 2.—The Relationship between the Potentials of Hydrogen and Oxygen Electrodes at Various Pressures and Acidities.

rate of hydrogen discharge is determined primarily, of course, by the driving force of the corrosion reaction, as indicated by the e.m.f. series. The rate of hydrogen removal from the cathode surfaces is determined by the rate of its diffusion away from the interface and by the concentration of oxygen which may be present at the interface. If the concentration of oxygen is more than sufficient to combine with all the hydrogen liberated, the cathodic areas are in reality functioning as oxygen electrodes. Theoretically, the maximum pressure which could be reached by such an oxygen electrode would be 0.21 atmosphere, the pressure of oxygen in air. The discharge of hydrogen gas below atmospheric pressure or the bubble point in the absence of the oxygen may be compared to the evaporation of water below the boiling point. Extending this analogy, the discharge of hydrogen on an oxygen electrode may be compared to the evaporation of water below the boiling point under reduced pressure, and the evolution of hydrogen gas bubbles corresponds to actual boiling of water.

It is now of interest to consider the electrochemical behavior of a metal electrode when immersed in a definite volume of pure water. Initially there are no metal ions in solution. It follows from the discussion that has preceded that the potential of the metal against its environment at the *instant* of immersion must be infinitely electronegative or in other words, the initial corrosion tendency is infinitely great. In consequence, hydrogen ions are forced out of solution on the cathodic areas, being replaced by the metal ions passing in at the anodic areas. The interfacial reactions involved take place with a speed approaching that of light, and within a fraction of a second after immersion the metal ion concentration at the surface of the anodes has passed through a sufficient number of tenfold changes to bring the potentials of all areas of the electrode surface well within the range of the e.m.f. series as usually defined.

Simultaneously with the increase in metal ion concentration, the hydrogen ion concentration decreases and the hydrogen pressure at the cathodic areas increases. The result is that the potentials of the metal and of hydrogen approach each other and may become and remain identical, under which circumstances corrosive action must cease. This may more readily happen, and with a minimum of corrosion, in a closed system, which permits the development of appreciable hydrogen pressures and consequently the maintenance of fairly electronegative cathode potentials. It may also happen in an open system (in the absence of oxygen) with the more electropositive metals, such as copper and silver. In these cases only an infinitesimal amount of corrosion is necessary to develop and maintain hydrogen electrodes of sufficient pressure to equal the anodic areas in potential. As a rule, however, metals cease corroding merely because their environments have become saturated with them before equality of the potentials of the anodic and cathodic areas is attained. This holds true not only for the more readily corrodible metals, such as zinc, iron and lead, but also for the semi-noble metals, if oxygen is present. If the diffusion of metal ions from the surface of a corroding metal is slow, corrosion may cease when only the environment immediately adjacent to the metal has become saturated. Protective films so formed result from the precipitation of metal ions as hydroxides or other, more insoluble compounds, in such close proximity to the metal surface that further corrosive action is retarded or possibly even prevented entirely. Such precipitation may be due solely to a paucity of aqueous environment. For example, a thin film of moisture on a metal surface may be rapidly converted by corrosion and evaporation, first to a saturated solution of the metal hydroxide, and then to the dry hydroxide or oxide. Subsequent similar wettings may serve to render the film of corrosion products thicker and more impervious. Obviously the oxygen, carbon dioxide and in some instances other gases in the environment may aid in precipitating the metal ions with the result that there may be developed a coating which is resistant to the solvent action of water.

This coating may be of such nature as to render the metal surface passive or, in effect, noble. Chromium does not readily corrode because it has already corroded so rapidly and so uniformly that the film of corrosion product formed does not mar its reflectivity. The electrochemical behavior of chromium indicates that its surface is not chromium but oxygen in some form. It seems entirely probable that the passive film consists of either a continuous layer of adsorbed oxygen or a continuous layer of closely packed chromic oxide, with each molecule so oriented that the oxygen is on the outside. Similarly in the case of iron it has been shown that passivity is associated with an oxide film. Electron diffraction studies indicate that this film when formed in air is composed of ferric oxide of a close packed structure in contrast to a film of ferrous hydroxide which is not so protective. In solution it seems likely that the degree of passivity of the iron surface is a function of the concentration of oxygen on the surface, and that the composition of the passive film may correspond to that of a definite oxide in which an indeterminate amount of oxygen may be dissolved depending upon the circumstances.

Thus far the discussion of corrosion mechanism has pertained to the origin of corrosion cells, their potentials and the function of corrosion products in determining the endpoint of the process. The rate of corrosion, that phase of the problem of most practical importance, is more complex. As previously stated it cannot be calculated but must be measured in some manner. The preferable experimental approach would be to measure the characteristics of individual corrosion cells, since the current which flows in these cells in a given time is a direct measure of rate of corrosion. While it is infeasible to do this, it is possible to determine the relative importance of those factors which increase and those which decrease the rate of corrosion.

The great speed of the primary electrode reactions has been referred to previously. Although metal ions dissolve and hydrogen ions are discharged at extremely high speeds, the secondary processes of diffusion and convection by means of which metal ions are removed from the proximity of the anode are relatively slow. As a consequence, the concentration of metal ions immediately adjacent to the anode is considerably higher than that which would exist if the solution remained uniform throughout, and the tendency for metal to dissolve in the film of solution at the anode surface is less than it would be if the solution were uniform throughout. This difference in solution tendency expressed in volts is known as anode polarization. In like manner, the decrease in hydrogen ion concentration at the cathode and the accumulation of discharged hydrogen at its surface gives rise to cathode polarization. Gas polarization, usually referred to as "overvoltage," is entirely analogous to metal polarization, with the exception that concentration of the product of electrolysis *within* the electrode is much more significant. It is obvious that polarization must increase with current density and, to a much lesser extent, with time. Polarization is a counter-electromotive force which invariably opposes the causative voltage.

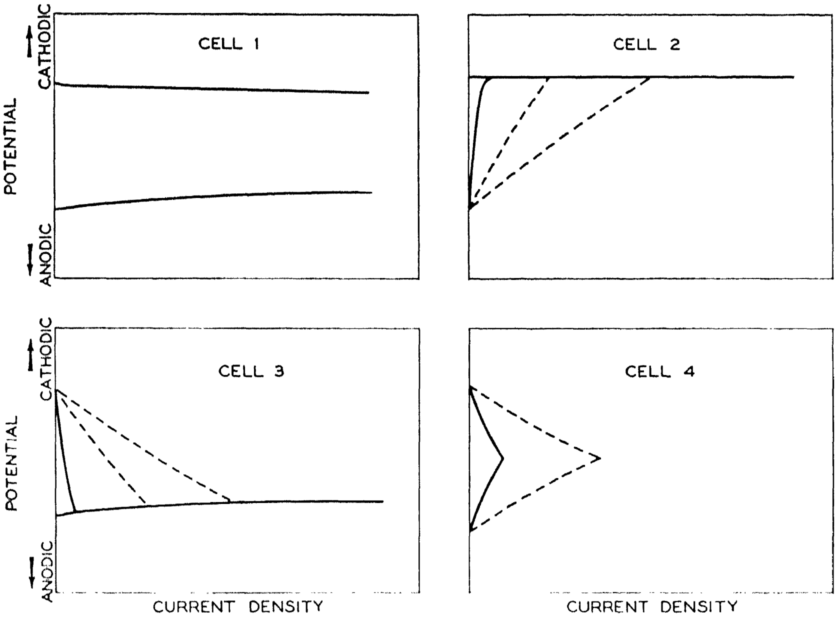


Figure 3.—Types of Polarization in Corrosion Cells.

This polarization behavior of corrosion cells largely determines the rate of corrosion. It is obvious that the effective voltages of corrosion cells may be reduced by polarization virtually to zero, in which case the rate of corrosion is limited to that required to maintain this polarization. In other words, the progress of corrosion may be controlled by the extent either of anode polarization or cathode polarization or both. Figure 3 represents the variety of current density-potential relationships which may exist in corrosion cells.[8] In Cell 1, in which there is no appreciable polarization of either anodic or cathodic areas (as indicated by the small change of potential with current), corrosion current flow is limited by the resistance of the electrolytic paths between anodes and cathodes; and since this may be small if these areas are contiguous, the corrosion rate may be high. In Cell 2 the anode is highly polarized as represented by the solid line, or progressively less polarized as the point of intersection with the non-polarized cathode occurs at higher and higher current densities, as represented by the dotted lines. In a similar way Cell 3 shows cathode polarization only and Cell 4 both anode and cathode polarization. Since the rate of corrosion is proportional to the flow of current per unit area it is obviously limited in the last three cases by the values of current density at which the polarization curves intersect. In the presence of adequate oxygen concentration or in cases where hydrogen is readily discharged, corrosion cells are likely to resemble Cell 1. Where this is not the case, as in the absence of oxygen or where the cathodes have high values for hydrogen overvoltage, the result will be as shown for the cathodically polarized Cell 3. The presence of an inhibitor such as a positively charged colloid or the amalgamation of the metal surface with mercury are other conditions which promote cathode polarization. On the other hand, the action of passivating agents such as chromates, silicates and in some cases sulfates, carbonates, etc., is to produce anodic polarization as in Cell 2. It will be observed that, whereas in the presence of inhibitors of the type mentioned above which polarize the cathode, the resulting potential of the corrosion cells and therefore of the metal specimen as a whole should move in the anodic direction as the process of inhibition takes place, in the case of passivating agents (which influence anode processes) the effect of increasing passivation is a trend of potential in the cathodic or noble direction. In both cases corrosion is retarded or prevented entirely. It is well to point out, however, that if the concentration of the passivating anion is inadequate to insure and maintain complete passivity there may be small insufficiently protected areas at which metal will dissolve, giving rise to pitting.[9] These areas may be so small as not to affect appreciably the composite potential of the metal under the conditions of measurement.

---

[8] Burns, R. M., *Bell System Tech. J.*, **15**, 20 (1936); see also, Evans, U. R., *J. Franklin Inst.*, **208**, 45 (1929).

The manner in which the conductance of the surrounding electrolyte influences the rate of corrosion is illustrated in Figure 4A, in which the upper curve represents the cathodic and the lower the anodic polarization. Assuming equal anodic and cathodic areas the corroding current density for the lower conducting solution is represented by M and that for the higher conducting solution by N. In the actual case where anodes and cathodes are in close juxtaposition, the internal resistance is low and consequently the corroding current density approaches that represented by the intersection of the polarization curves.

Thus far consideration has been confined for the sake of simplicity to corrosion cells in which the anodic and cathodic areas are equal. Usually in actual experience this is not the case. In corrosion characterized by pitting, the anodic area is generally small compared to the cathodic areas. This situation is illustrated in Figure 4B, in which it will be seen that under these conditions a high corroding current density corresponding to a rapid rate of attack may occur. Conversely, in cases where the ratio of anode areas to cathode areas is large, the rate of attack per unit area will be slow, being thus controlled by cathodic polarization.

---

[9] Mears, R. B., *Discussion Trans. Electrochem. Soc.*, **69**, 181 (1936).

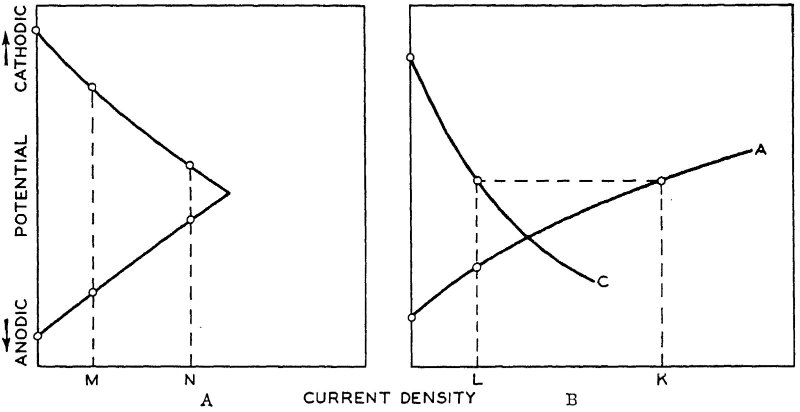


Figure 4.—Effect of Conductance and of Electrode Area on Corrosion Current Densities.

M = Lower Conducting Solutions.
N = Higher Conducting Solutions
L = Corrosion Current Density for Cells of Equal Cathode and Anode Areas.
K = Corrosion Current Density When Ratio Anode Area to Cathode is Small.

In this connection it may be of interest to consider the effect of impurities upon rate of corrosion. If the contaminating metal is anodic and exists as a separate phase it will tend to dissolve with the formation of small pits which, having once formed, may possibly continue to function as the anodes of oxygen concentration cells. If, on the other hand, the metallic impurity is cathodic and is present as a separate phase, corrosion will be rather more uniform in character, and its rate will be controlled in the absence of oxygen by the ability of the impurity to discharge hydrogen. Unless its overvoltage is low, that is, unless it discharges hydrogen readily, the rate of corrosion will be slow, the corrosion cells being polarized cathodically. The presence of oxygen or oxidizing agents under these conditions will depolarize these cathodic areas and accelerate corrosion.

From the foregoing it is apparent that a knowledge of the anodic and cathodic current density-potential relationships which are established on the surface of a metal in a given environment would make possible an understanding of the processes which are taking place and lead to a prediction of corrosion behavior. It is generally impossible to measure these quantities as they relate to individual corrosion cells, owing to a lack of knowledge of the electrode areas involved. By ingenious laboratory methods this can be done in certain cases however.[9a] Probably these electrode areas vary widely in size, and change in size with the progress of corrosion. Sometimes the nature of the cathode is also uncertain. Practically, however, it is a simple matter to determine a composite of the resultant potentials and their change with time. These time-potential measurements indicate whether the process is anodically or cathodically controlled and in some cases furnish information as to the rate at which it is proceeding, experimental facts which are of value in predicting corrodibility.[10] A recording potentiometer is of considerable assistance in this connection.

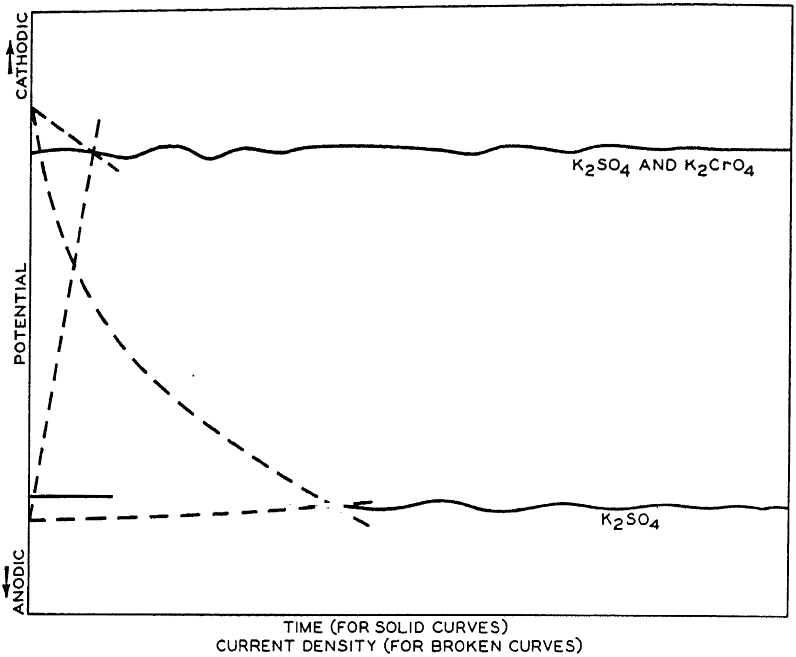


Figure 5.—Time-Potential Relationship of Iron in K_2SO_4 as Affected by Addition of K_2CrO_4.

Figure 5 illustrates schematically the correlation between these time-potential relationships and the anodic and cathodic polarizations which determine their positions. It will be seen that the potential of iron in a solution of potassium sulfate (represented by the lower solid curve) is essentially the potential of iron in the solution, the cathodic areas being polarized. When potassium chromate is added to the solution the resultant potential of iron is shifted markedly in the cathodic direction, the position being determined by anodic polarization. The actual values of the potential of iron in these cases are of the same order as that of iron alloyed and rendered passive by the addition of chromium and nickel.

[9a] Brown, R. H. and Mears, R. B., *Trans. Electrochem. Soc.*, Preprint 74-2 (1938).

[10] May, R., *J. Inst. Metals,* **40,** 152 (1928); Bannister, L. C. and Evans, U. R., *J. Chem. Soc.*, 1363 (1930).

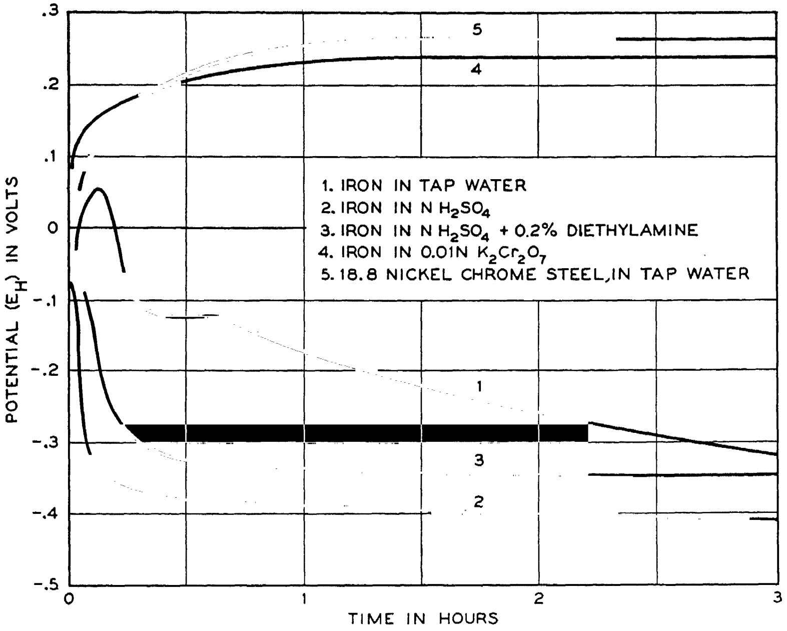


Figure 6.—Potentials of Iron and Stainless Steel in Water and Certain Solutions.

In Figure 6[11] is shown the actual time-potential behavior of specimens of iron and 18-8 chromium-nickel steel immersed in water and certain solutions. It will be observed that the potential of iron in normal sulfuric acid rapidly becomes electronegative. The initial trend of a similar specimen immersed in tap-water is toward the noble side, owing probably to the passivity of the air-formed film. Within a few minutes, this trend is reversed, the specimen becoming more electronegative probably because of the destruction of this film. In the presence of an oxidizing solution, potassium dichromate, it will be seen that the potential of iron (represented by curve 4) becomes markedly electropositive. A similar passive behavior is shown by stainless steel in tap-water (curve 5). The iron specimens, the potentials of which are represented by curves 1 and 3, displayed active corrosion, but iron in potassium dichromate solution (curve 4) and stainless steel in water did not corrode. In other words, a trend in the electronegative direction, which as mentioned before is characteristic of cathodic polarization, is associated with active corrosion, whereas the electropositive trend of potential is indicative of passivation. It is of interest to note in this connection that certain organic compounds used as corrosion inhibitors which, as previously mentioned, function by retardation of the cathodic reaction, appear to have little or no influence on the characteristic of time-potential curves. The experiment represented by curve 3, for example, differs from that of curve 2 only by the presence of 0.2 per cent diethylamine, a typical corrosion inhibitor. Corrosion has been greatly retarded in this case but the iron is still in the active or corroding class.

---

[11] Burns, R. M., *J. App. Phy.*, 8, 398 (1937).

The foregoing discussion of the principles of corrosion has outlined the mechanism by which metals corrode. Later chapters will seek to apply these principles in more detail in discussions of the performance of coatings of various kinds. Detailed discussion of methods of measuring rates of corrosion is given in Chapter 12. It will be evident in discussing metallic coatings that insofar as these coatings are continuous the behavior of the coated surface will be practically identical with that of the coating metal in solid form. When, as is more often the case, the coating contains or developes pores, galvanic couples of dissimilar metals arise. In terms of these couples, metallic coatings fall into two general classes: those in which the coating metal is the anodic member of the couple, as in the case of zinc coatings on iron and steel, and those in which the coating metal is cathodic, as illustrated by copper, lead, and in some cases, tin coatings, on ferrous metals.[11a]

Anodic coatings protect the basis metal by changing exposed areas of it from anodes to cathodes; in accomplishing this result dissolution of the coating occurs. This sacrifice of the coating may continue until its complete dissolution. Before that point is reached it will be observed that the portions of the exposed basis metal most remote from the disappearing coating metal will begin to corrode. In other words there is a limit to the size of the area which, under given conditions, will receive cathodic protection; beyond that limit local corrosion cells begin to function.

Considerable attention has been given in recent years to the use of cathodic protection for the preservation of large structures such as pipe lines, boilers and lead-sheathed cables, and some reference will be made to this in a later chapter. The subject has received theoretical treatment by several investigators.[12]

[11a] For a lucid discussion of the anodic-cathodic relationship of metallic coatings, see Hoar, T. P., Paper before Electrodepositors' Tech. Soc. (London), Oct. 20, 1937.

[12] Jensen, C. A., *J. Soc. Chem. Ind.*, **15**, 547 (1896).
Bauer, O., and Vogel, O., *Mitt. Kgl. Materialprüfung*, **36**, 114 (1918).
Evans, U. R., and Stockdale, J., *Metals and Alloys*, **1**, 377 (1930).
Evans, U. R., *Metals and Alloys*, **2**, 62 (1931).
Mears, R. B., and Brown, R. H., *Trans. Electrochem. Soc.*, **74**, (1938).

Coatings of metals which are cathodic to the basis metal may show pinhole corrosion, each pore becoming a pit which penetrates, and may in time perforate, the basis metal. It is for this reason that every effort is made in the production of this type of coating to secure a non-porous metal layer. The highly protective character of such coatings when pore-free is attributable, as mentioned earlier, to the corrosion resistant quality of the superficial films which develop upon their surfaces.

Organic coatings act as physical barriers which exclude more or less effectively the corrosive elements of the environment from the metal surface. Both moisture and oxygen permeate the coating, however, with the result that the basis metal may corrode. As will be shown, various surface treatments of the metal, such as phosphating and the use of inhibitive pigments, may retard or even prevent corrosion for considerable periods of time.

INDIAN INSTITUTE OF SCIENCE
LIBRARY
BANG

3169

IISc Lib B'lore
540.0202 N21.79

Chapter 2

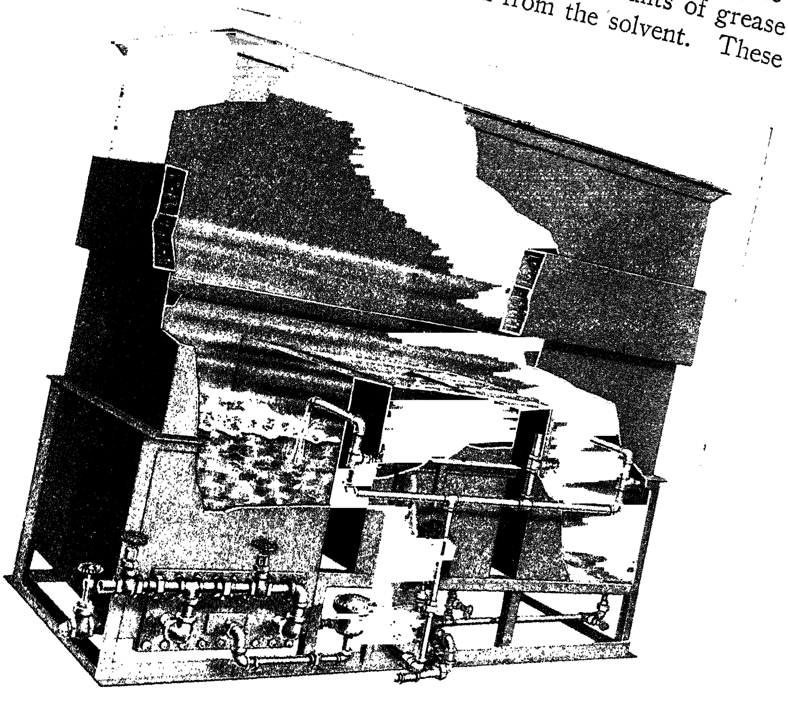
Surface Preparation for the Application of Coatings

The chemical and physical nature of a metallic surface has a very marked effect upon the quality of any coating applied to the surface. It is well known that the presence of grease, corrosion products, dirt, and extraneous materials affects the adherence and continuity of coatings whether of metallic or organic nature. The physical structure of the surface influences the adhesion, and, in the case of metallic coatings, the porosity, uniformity, and smoothness of the coating. In general, it may be said that the character of a coating is no better than the surface to which it is applied, and consequently it has come to be recognized that the production of protective coatings of high quality is dependent upon the proper and thorough pretreatment of the surface of the basis metal.

The preparation of a metal surface for coating may involve three steps. There is first the removal of grease and other contamination, usually followed by a pickling or sand or shot-blasting operation to remove oxide scale and corrosion products, and finally, in some cases, an etching, graining, polishing or buffing treatment may be employed to secure adhesion or to obtain appearance characteristics desired in certain metallic coatings. A great variety of practices has arisen to accomplish these ends and the choice of the procedures which are employed is determined largely by the character and volume of the work to be finished and the economics of alternative processes in given localities. A general outline of surface preparation methods will be given here, and further details of some of the processes will appear later in connection with the application of specific coatings.

Metal parts, upon reaching the finishing department, are nearly always contaminated with grease derived either from slushing oils employed for temporary protection during storage or from cutting or buffing compounds used in drawing, machining, threading and surfacing operations. In other cases lubricating oils and greases, together with soot and dirt, may be the principal type of surface pollution. The oily substances fall in general into two classes, animal or vegetable fats and mineral oils. The former are removable upon saponification with strong alkalies, while the latter class is effectively removed by emulsification with soaps, soap substitutes, such as the alkali salts of sulfonated naphthalene or higher alcohols, and other substances capable of reducing the surface tension of water. Many organic solvents dissolve both classes of oily substances.

An important new development in solvent degreasing[1] is the use of chlorinated hydrocarbons, notably trichlorethylene, under conditions in which the vapors are allowed to condense on the surface to be cleaned, removing thereby the greasy materials in the drip of the condensate. The use of petroleum-base solvents has been rather limited, owing to the fire hazard involved, and the fact that objectionable amounts of grease remain on the surface after removal of the work from the solvent. These limitations are avoided in the use of trichlorethylene vapor. The process, moreover, is well adapted to automatic operation. While the equipment for carrying out the process consists essentially of a heating chamber for the liquid, a vapor compartment (in which the work is cleaned) and a condenser, in the form of cooling coils, for controlling the vapor level in the apparatus, it has been found advantageous in many cases to include pro-



Courtesy of Detroit Rex Products Company.

Figure. 7.—Three-dip trichlorethylene degreaser which gives straight-line sequence of cleaning operations, consisting of immersion in boiling solvent, immersion in clean cooling rinse, and final vapor rinse.

---

[1] Davidson, W. W., *Trans. Electrochem. Soc.*, 72, 413 (1937).

vision for immersion in the liquid solvent before exposure to the vapor. There is shown in Figure 7 [2] a cut-away view of a three-stage trichlorethylene degreaser of the type now being widely used in industry.

In the operation of the three-dip degreaser, the work passes on suitable conveyors into the boiling solvent, where the bulk of the grease is removed, then into a chamber of cold purified solvent, and finally through solvent vapor. The condensate from the condenser is fed back into the reservoir which supplies the chambers with liquid solvent, thus continually purifying the liquid. The speed of the conveyor is usually from 6 to 8 feet per minute. In cases where conveyor operation is not justified, the work may be hand-dipped, employing baskets or racks.

Immersion in hot alkaline solution is the most common method of cleansing metal surfaces. It is made more effective by the application of current, making the parts to be cleaned cathodic. Under such conditions, high concentrations of free alkali are maintained at the surface, and the copious evolution of hydrogen causes agitation and aids in the emulsification of the oily substances present. Electrolytic cleaning of this type has been extended recently to the strip metal industry as a means of removing rolling oils from strip to be used in the manufacture of tin-plate.[3] In this process, coils of 5000 feet of strip, 36 inches wide and 0.010 inch in thickness are degreased at rates up to 900 feet per minute, employing a hot solution of the ortho- and meta-silicates of sodium and a current density of about 1 ampere per $dm.^2$ (10 amperes per sq. ft.)

There is considerable variation in cleaning procedures. In some cases the work is dipped in one hot alkaline solution and electrocleaned in another solution. The work is sometimes made anodic for a portion of the time in the electrolytic cleaner.

Soda ash is one of the principal constituents of most alkaline cleaners. Caustic soda is added in small amounts to saponify fatty substances, and soaps are widely used where the oil to be removed is of the mineral type. Sodium phosphate, borax, and sodium silicate are further examples of suitable reagents for metal cleaning.

The removal of oxide scale is accomplished either by acid pickling or by mechanical abrasion of the surface. The pickling operation consists in immersing the metal in dilute acid until the mill scale has been loosened or dissolved. The usual practice is to use from 4 to 5 per cent sulfuric acid at about 65 to 75° C. (149 to 167° F.), although hydrochloric acid of various concentrations is employed to a limited extent. Inhibitors are used, particularly with sulfuric acid, to minimize the attack of the acid upon the metal. These are usually organic substances, such as glue, pyridine, and sulfonated oils, which, as is stated in a more extended discussion in Chapter 4, appear to restrain dissolution of the metal by inducing cathodic polarization.

---

[2] Courtesy of the Detroit Rex Products Company, Detroit, Michigan.

[3] Stone, M., *Metal Cleaning and Finishing,* **9**, 988 (1937); **10**, 20 (1938).

An initial dip in hydrofluoric acid is sometimes used in pickling sand castings. A variety of scaling or acid dips is employed for removing tarnish and oxide from brass and bronze. These are usually mixtures of sulfuric and hydrochloric acids containing small proportions of nitric acid.[4]

For the preparation of iron and steel surfaces for painting it has been found advantageous to pickle in phosphoric acid solutions.[5] Owing to the cost of this acid, the more usual practice is to descale first in sulfuric acid and follow by a dip in 2- to 10-per cent phosphoric acid containing usually a fractional per cent of iron. The priming paint is applied directly to the phosphated iron surface. It is not common practice to pickle structural steel.

Anodic pickling is employed to a certain extent as a means of increasing the rate of pickling and at the same time of bringing about a mild etching of the metal surface suitable for the application of heavy electrodeposited coatings. In this case a 25- to 30-per cent solution of sulfuric acid is suitable, employing about 150 amperes per sq. ft.[6]

Sandblasting has long been a favorite method of oxide removal, particularly where a slightly roughened surface is desired for the improvement of adherence of coatings. Steel grit and shot have replaced sand to a considerable extent as abrasives. In operation, the abrasive is introduced into an air stream at air pressures of from 25 to about 100 pounds per sq. in., and the blast directed over the metal surface until the oxide scale is removed. In automatic conveyor type machines for blasting, the nozzles are so arranged as to provide a more or less uniform blasting of the surfaces of the parts. The process of blasting is said to induce a certain amount of surface hardening. A comparison of the relative roughness of the surface produced by blasting with various sizes of steel grit is shown by means of profilographic records in Figure 68 in Chapter 14.

A widely practiced method of scale removal from stock which has undergone weathering is by scratch-brushing with wire brushes, either hand or machine operated. Weathering serves to loosen mill scale by under-rusting. A fairly uniform, finely scratched surface may be produced upon metals by this means. The rotating wire brush method has recently been investigated in some detail.[7] It was found that it is possible to remove hard scale from a steel surface provided the steel wire of the brush is hard enough, of proper size, and provided considerable pressure is applied. Under certain conditions of operation the mill scale was merely burnished. It is an impractical method of descaling unless the surface has been previously weathered.

A grinding operation employing a solid wheel of hard, relatively coarse abrasive, either silicon carbide or fused alumina, is sometimes used to remove hard mill scale. This method is also in common use as a means of removing fins, burrs, and machine marks on fabricated parts.

---

[4] Graham, A. K., *Trans. Am. Electrochem. Soc.*, 52, 289 (1927).

[5] Footner, H. B., Corrosion Committee of Iron and Steel Institute, Fifth Report, p. 369, 1938.

[6] Hall, N., *Monthly Rev. Am. Electroplaters' Soc.*, 24, 905 (1937).

[7] Corrosion Committee of Iron and Steel Inst., Sec. E3, p. 355 (1938).

Polishing and buffing are employed for the production of uniform smooth surfaces where it is desired to obtain electroplated coatings with such characteristics. These operations may be used also for surface finishing as, for example, on nickel coatings before the application of chromium, or as a finish for brasses, bronzes, etc. Still another process used mainly to remove surface roughness and to produce a luster on metal parts and metal-coated parts is ball burnishing. This is carried out in a rotating barrel using hardened steel balls, jacks or cones and a special soap solution.

Polishing and buffing are somewhat similar operations, the second following the first where high luster or color is desired. Both processes employ revolving wheels. Polishing wheels are made from felt, walrus hide, leather, sewed cotton buffs, etc., which are coated on the outside surfaces beforehand with abrasives, such as emery, corundum or fused alumina, held in position by glue.[8] Solid discs of wood or metal, over which is slipped a sleeve faced with abrasive, comprise another type of polishing wheel. Lubricants may be used in polishing with wheels of either kind.

Buffing wheels are generally composed of sewed cloth or canvas. The abrasive in this case is not a part of the wheel, but is applied to the wheel intermittently from a bar or cake containing its own binder, which may be rosin with tallow or petrolatum. Among popular abrasives for buffing are tripoli (largely silica from the weathering of quartz-bearing rock), rouge and crocus grades of ferric oxide, pumice, Turkish or American emery, whiting and Vienna lime (calcined dolomitic limestone).

---

[8] Garner, C., *Monthly Rev. Am. Electroplaters' Soc.*, 25, 96 (1938).

Chapter 3

Types of Metallic Coatings and Methods of Application

HISTORICAL

Man has devised many methods of coating one metal with another. The ancients plated and inlaid base metals with gold, silver, and a mixture of the two known as electrum. These noble-metal coatings appear to have been hammered over the surfaces of bronze, copper or iron which were previously heated. The elder Pliny described "fire gilding" employing gold amalgam. The Romans coated copper vessels with tin, probably by immersing them in the molten metal. Coating sheet-iron with tin is of much more recent origin, although it was a well established art for a century before the appearance of hot-dipped zinc coatings about 1740. Sheffield plate, produced by fusing sheet silver on copper or brass, was discovered about 1743 and for a hundred years was a prosperous industry, finally being largely superseded by electroplating. Gold and silver plate of this type are now made by soldering or welding the coating to the base metal. Coating metals with gold leaf and gilding with gold powder suspended in a liquid are old arts. The early electroplating operations were of the "dip-gilding" type in which base metals, immersed in solutions of gold, silver or platinum salts, become coated with very thin films of the noble metal by replacement. This process is still widely used in the production of cheap jewelry. Another type of contact plating described in a reference book for "the manufacturer, tradesman, amateur and heads of families"[1] consisted in zincing or tinning copper and brass vessels by boiling them respectively in solutions of zinc salts containing zinc turnings or tin salts containing tin turnings. Following the invention of the voltaic cell electroplating in the modern sense came to be practiced. Silver, gold and zinc were first electrodeposited in 1840 and platinum in the next year. Later copper, nickel, tin and lead and finally most of the common metals except aluminum and magnesium have come to be electroplated as firmly adhering coatings from aqueous solutions.

Since the beginning of the present century a number of new metal coating processes have been devised. Of these, the most important commercially are cementation, metal spraying and "metal-cladding." Cementation is a means of surface alloying and finds numerous metallurgical applications which depend upon the modification of the surface of a metal, the most familiar of which is the important process of "case hardening" of steel. Other examples are "sherardizing" in which the surface of an iron article is zinc-coated and "calorizing" in which the coating is aluminum. Metal-spraying consists in atomizing molten metal by compressed air or by some mechanical device, forcing it through a nozzle at high velocity and allowing the resulting spray to impinge on the surface to be coated. Most of the common metals and alloys can be sprayed, but zinc, tin, aluminum, copper, lead, iron and brass have been used to the greatest extent. Almost any desired thickness of coating may be obtained by this process. "Metal-cladding" is a term used to describe the method of coating one metal with another by rolling the two metals in intimate contact with each other. Coherence of the two metals is induced either by soldering, electro-welding, or casting one in contact with the other previous to the rolling operation. By this mechanical process steel for example is coated with copper, nickel or with alloy steels.

---

[1] Cooley, "Cyclopedia of Practical Receipts," 532, 576, New York, Appleton & Co., 1846.

Two other metal coating processes to attain limited commercial application recently are dependent upon the condensation of metal vapor in a partial vacuum. In cathode sputtering, the more widely used of the two, the coating metal is evaporated from the cathode during a glow discharge induced in a chamber at a pressure of 0.01 to 0.1 mm. of mercury and a voltage of from 500 to 2000. In the other process the coating metal is vaporized by heating it in a vacuum of 10^{-4} mm. of mercury. In both processes condensation of the metal vapor usually occurs on the walls of the chamber as well as upon the surface to be coated.

IMMERSION IN MOLTEN METAL: "HOT-DIPPING"

One of the oldest and most familiar of the commercial processes of applying metallic coatings to other metals is that known as "hot-dipping." Essentially this process involves immersing bodily the article to be coated in a bath of molten metal for a short time; usually very little, if anything, additional is done to change the properties of the metal coating which adheres to the surface upon removal of the article from the molten metal bath.

Principles

For the successful coating of one metal with another by means of the hot-dipping process, it is necessary that the two metals alloy with each other, at least to some extent. A clean glass rod when dipped into water and withdrawn is found to be covered by an adhering film of moisture, the force of surface tension serving to make this film uniform over the surface which was wetted. The production of a metal coating by immersion in a bath of molten metal is not strictly analogous to this simple illustration, however, but is more like the case of the immersion of a crystal of rock salt in water. The film which covers the surface in this case is not one of pure water, but contains an appreciable proportion of the salt in solution. Because of the tendency of the substance to dissolve, it is decidedly easier in this case to produce a uniform coating film over the surface of the immersed crystal. The dissolving of the small proportion of salt by the enveloping film of water is strictly analogous to the alloying action which occurs during the hot-dipping coating process and makes this process a successful one for coating metals. Alloying of iron with molten zinc or tin is generally regarded by the men engaged in the zinc or tin coating industry as a more or less unavoidable nuisance incidental to the process. It is not generally recognized that, fundamentally, success in this process is attained almost entirely because of this behavior of the two metals.

In most cases of the commercial coating of metals by hot-dipping, the coating metal, zinc, tin, or aluminum, for example, alloys very readily with the "base metal," that is, the metal to be coated, for example, iron. In case the coating and base metals do not alloy directly, the same end may often be accomplished by the use of a small amount of a metal which does alloy with both of the others. This is usually done by making a suitable addition to the molten metal bath, though the same result may be attained if the "addition" is made as a surface film on the base metal before immersion in the molten metal. As will be explained later, although there is no mutual alloying whatsoever between the metals lead and iron, lead coatings on iron and steel are often secured by this means.

Although hot-dipping is essentially a method depending upon surface alloying, it should not be inferred that no coating whatever can be obtained if alloying between coating and base is lacking. Just as a film is produced over the surface of a clean glass rod when immersed in water, so also, if a clean metal surface, for example, iron, is brought into contact with a clean molten metal with which it does not alloy, lead for instance, a continuous coating film of the latter can often be made to cover the surface. The difficulties in producing such a continuous coating under these conditions are so great, however, as to render the process impracticable. Much of the difficulty arises as a result of the tendency of the coating during its solidification to coalesce more or less into globules, thus giving rise to breaks in the coating. This tendency is counteracted by the alloying action between the coating metal and the base.

The necessity for some alloying action between coating and base metals, in the hot-dipping coating process, is two-fold, therefore, although the second may perhaps be considered as a corollary of the other. First, slight alloying of the two insures a complete initial "wetting" of the surface of the base metal and therefore a uniform spreading of the molten metal over the surface; and secondly, as a result of this, the adhering film of metal solidifies without exhibiting any pronounced tendency to draw away from the base.

General Nature of Hot-Dipped Coatings

In no case is a metal coating which is produced by the hot-dipping process a simple film of the pure coating metal. As an unavoidable consequence of the necessary mutual alloying action, the coating must always be contaminated more or less with traces of the base metal, and its structure and properties must be somewhat different from those of a similar layer of the pure metal.

In structure a hot-dipped coating always shows evidence of at least two more or less distinct layers, the inner one being usually referred to as the "alloy layer." The metals used for coatings in the hot-dipping process are decidedly different in most of their properties from the base metals which are to be coated. The alloys formed by the union of unlike metals are usually not of a simple type, such as simple solid solutions or plain eutectic series, but of the more complex types in which intermetallic compounds occur. The inner or alloy layer of a hot-dipped coating is practically always made up in large measure of an intermetallic compound of the two constituent metals. Consequently this part of the coating is harder and more brittle than the outer layer which consists largely of the pure coating metal.

When a metal of high melting point, such as iron, is immersed in a molten metal of low melting point with which it alloys, such as zinc or tin, traces of it dissolve in the melted metal in the same way that salt dissolves in water. At the same time the molten metal combines with and diffuses to some extent into the solid metal, giving rise to a definite alloy layer. If the process is allowed to continue the diffusion may extend inward far enough so that a second layer forms, which is different from the first in its composition and properties. It is a singular fact that the alloy layers formed in this manner do not gradually merge, one into the other, but each is of a quite definite composition, and the change from one layer to the next is a decidedly abrupt one. When the immersed specimen with its outer alloyed surface is removed from the metal bath, it carries with it a surface layer of molten metal which by solidifying forms the outer layer of the final coating.

The relative thickness of the alloy layer in any hot-dipped metal coating varies with the kind of coating. For example, in a tin coating on iron this layer is very thin, whereas in a zinc coating on iron the alloy layer may under some conditions constitute the greater part of the coating. Since the amount of alloying in any case depends also upon the time, the temperature, and the mass of the parts, all these factors must be carefully regulated in practice. Prolonged immersion in the molten metal results in the formation of a thick alloy layer which renders the coating so brittle that for many purposes it may be useless.

Practical Aspects of the Hot-Dipping Process

In the simplest applications of the hot-dipping process, very little equipment besides handling tools and a container for the molten metal is required. For the coating of vast quantities of sheet and wire, however, which is done almost exclusively by this process, very elaborate mechanical devices have been developed. These are referred to briefly in later chapters.

Hot-dipped coatings are almost always relatively thick as compared with most other types of metallic coatings. In many respects, however, the hot-dipping process is somewhat wasteful of metal since there is no way of controlling accurately the amount of coating metal used and its distribution over the surface. In the case of materials of regular shape, such as sheet and wire, the uniformity of the coating can be fairly well regulated mechanically and the excess metal wiped off. With small pieces—nails, bolts, screws, and the like—a hot centrifuging is used to advantage in regulating the amount of coating metal left on; but for the great majority of pieces there is no simple and sure method for regulating both the amount of metal used and its distribution as a coating over the surface.

The hot-dipping process is a commercial success only with metals of relatively low melting point. For zinc and tin coatings and for some of the lead alloy coatings, its use forms the basis of one of the leading industries. Of the other metals of lower melting point, aluminum (m. p. 658.7° C., 1218° F.) is the only one which is used, and this only to a very limited extent. The production of cadmium coatings (m. p. 320.9° C., 609° F.) by hot dipping has not been seriously considered on account of the limited production of this metal. The difficulties involved in handling molten metals of high melting point, such as copper, nickel, or cobalt, in the large amounts necessary for the process have not encouraged experiments in the application of coatings of these metals by this process. The detrimental effect of the high temperature involved, if such coating metals were used, upon the properties of the metals to be coated is also a factor which is not encouraging.

Extension of the Hot-Dipping Process

If, instead of totally immersing the article to be coated in molten metal, a small amount of the coating metal is melted on the surface to be covered and then rubbed thoroughly over the surface, a coating can be produced which, in its essential respects, is the same as a hot-dipped coating. The tinning of copper sheets and containers is usually done in this manner. A slightly modified process consists in applying the coating metal as a powder, either dry or mixed into the form of a paste with a substance which serves the double purpose of binder and flux. When heated, the paste melts and under the influence of the flux spreads as a thin film over the surface. Lead, tin and zinc, as well as mixtures of the three metals, and silver appear to be the most suitable materials for this application. The process is of very limited commercial importance in the coating of metals although it is coming to be used as a means of repairing damaged coatings, particularly zinc coatings on steel structures or other large surfaces.

CEMENTATION

The characteristic feature of cementation, like that of hot dipping, is an appreciable alloying action of the surface layer of the treated metal.

Unlike hot-dipping, it does not necessitate the use of molten metal but consists in heating the metal while surrounded by another metal or non-metal, generally in a powdered form, to a temperature somewhat below the melting point of the more fusible of the two.

The process is of rather wide metallurgical application and was well known in ancient times. Copper, for example, was converted into brass by heating it in certain "favorable earths." Steel was made by heating iron in contact with charcoal. The latter process suitably controlled is, of course, the basis of the modern operation of "case hardening." By heating a soft, ductile (low-carbon) steel to a temperature of 870-900° C. (1600°-1650° F.) while it is surrounded by a carbonaceous packing material, the metal at the surface is converted to a considerable depth into a high-carbon steel by combining chemically with carbon which diffuses into it in the form of a gaseous compound. In the carburization of small parts in large volume the process may be carried out directly in gases, usually mixtures of carbon monoxide and hydrocarbons. Analogous to the carburization of steel is the nitrogen case-hardening process in which the surfaces of steel parts are hardened by heating to 925-1000° C. (1700-1830° F.) in a nitrogenous medium, usually ammonia gas. Nascent nitrogen liberated by decomposition of nitrogen compounds reacts readily with aluminum, chromium, vanadium, titanium, tungsten, manganese, molybdenum, etc., which may be present in the steel, forming dispersed nitrides and thereby surface-hardening the materials. Still another cementation process of surface hardening of steel consists in immersion in molten sodium cyanide at 850-870° C. (1560-1600° F.) The hardening produced by this treatment is more superficial than that obtainable in carburizing and nitriding and is due to the penetration of both carbon and nitrogen. These alloyed surfaces on steel are designed primarily, of course, for resistance to wear, although nitriding appears to be of some value in the prevention of corrosion.[2] The principle of cementation is, however, of considerable importance in producing coatings for the protection of metals against corrosion, and it is with this aspect that the present book is concerned.

Mechanism of the Process

It has long been known that certain metals diffuse into certain other metals merely upon contact at temperatures below their melting points.[3] Faraday and Stodart in 1820[4] observed that platinum alloys with iron upon the annealing at low temperatures of mixed powders of the metals. In 1868 Tohernoff showed that when two pieces of steel of similar nature are heated to about 900° C. in intimate contact they cohere. Experiments by Spring in 1882 indicated that alloying of metals may take place at ordinary temperatures merely by compression of the constituent metals, but Masing[5] several years later found that the function of pressure in this case was merely that of bringing the metals into more intimate contact. It was shown[6] in 1894 that very considerable alloying by cementation results if the ends of two carefully surfaced cylinders of a metal are pressed together for several hours at temperatures of from 200° to 400° C. That zinc readily alloys with an iron surface at relatively low temperatures was discovered accidentally in 1900 when zinc dust was used in the annealing of some iron and steel samples.[7] In recent years cementation coatings on iron have been produced with a great variety of metals and in some cases more than 1500° C. below their melting points.

---

[2] Homerberg, V. O., and Walsted, J. P., *Trans. Am. Soc. Steel Treat.*, **16**, Suppl. 67 (1929); Malcolm, V. T., *Trans. Am. Soc. Steel Treat.*, **16**, Suppl. 205 (1929); Sergeson, R., and Deal, H. J., *Trans. Am. Soc. Steel Treat.*, 18, 474 (1930).

[3] For review and discussion of the subject of diffusion in solid metals see: Mehl, R. F., *Trans. Am. Inst. Mining Met. Eng.*, 122, 11 (1936); Krynitsky, A. I., *Met. and Alloys*, 8, 138, 173 (1937).

[4] Faraday, M., and Stodart, J., *Quart. Jour. Sci.*, 9, 319 (1820).

It is evident from these observations that metals may interpenetrate merely upon intimate contact. In most cases the cementing metal has an appreciable vapor pressure at the temperature employed in the coating process and it is likely that at least some of the metal transferred to the surface of the base metal passes through the vapor phase. Both factors, contact of the metals and the presence of metal vapor, undoubtedly contribute to building up the coating as the process is carried out commercially. It is well known in zinc cementation that the intimate contact secured by "tumbling" the article being heated within the packing of zinc powder is necessary to secure uniform coatings. The presence of oxide films on the surface of a metal may retard or prevent cementation.

The penetration of the cementing metal into the surface of the base metal may occur in one or more of the following ways depending upon the nature of the metals involved, the temperature, duration of exposure, physical state of the base metal, orientation and size of crystals, pressure and character of contact: (1) by transfer through a solid solution, (2) by formation of an intermetallic compound, and (3) by migration along crystal boundaries.

Character of the Coating

A coating produced by cementation is simply a surface alloy layer of the base and coating metals. In most essential respects, it is comparable to the inner or alloy layer of a hot-dipped coating of the same metal. The coating metal, as such, does not enter into the structure of the coating except as particles may be mechanically entrained perhaps as a result of partial fusion resulting from too high an operating temperature.

It is characteristic of the process of cementation, at least for those metals which are capable of forming definite compounds with each other, that the alloy layer produced is not one in which the composition changes gradually from that of the "cementing" metal on the outside to that of the base metal on the inside. On the contrary, the coating is composed of sharply defined layers each of which is quite homogeneous, at least in its visible structure. Copper cemented with zinc dust forms an excellent demonstration of the structure of such coatings, on account of the difference in color of the different layers which form.[8] The outer silvery gray layer is much higher in zinc than is the inner one, which is a brilliant golden yellow, adjacent to the copper base. The relative thickness of the layers which make up the coating, and hence the average zinc content of the coating, is determined largely by the cementation temperature.

---

[5] Masing, G., *Zt. anorg. Allgem. Chem.*, **62**, 265 (1909).

[6] Spring, W., *Zt. Phys. Chem.*, **15**, 65 (1894).

[7] Cowper-Coles, S., *Engg.*, **118**, 277 (1924).

Alloy coatings are considerably harder and more brittle, as a rule, than those of the pure metal, and the chemical resistance is not the same as is that of the pure metal. In any comparison of the relative merits of coatings of the same metal made by different processes, for example, zinc coatings made by cementation and by electroplating, it should be borne in mind that metallurgically the two are of entirely different natures.

Practical Applications

The commercial production of protective coatings by cementation has been limited, until recently at least, to "sherardizing" by zinc powder, "calorizing" by aluminum powder and "chromizing" by means of chromium powder. Cementation by cadmium has been carried out successfully.[9] It has been shown [10] that in a similar fashion cementation coatings on steel may be produced at temperatures of 900° to 1200° C. with tungsten, vanadium, cobalt, uranium, titanium, silicon, zirconium, molybdenum, tantalum, boron, manganese [11] and beryllium.[12] Cementation with silicon was described more than twenty years ago [13] and has continued to interest investigators, the most recent development being the production of coatings by a process known as "Ihrigizing".[14] Many of these coatings display marked resistance to corrosion and it seems likely that they will come to be used on a commercial scale for the protection of ferrous metals. Although these cementation processes are used almost exclusively in the production of coatings on iron and steel, their application to other metals is apparent.

The cementation process, although particularly well adapted for small pieces, cannot very well be carried out on a small scale. The pieces are packed in the cementing metal powder in rather large containers which can be made fairly gas-tight and can be rotated about one axis so as to tumble the cementing powder over the surfaces to be coated. The whole must be heated for several hours and this is done by gas or by means of electric heating coils in the walls of the container. In some cases, as in calorizing, the process must be carried out in the absence of air, usually in an atmosphere of hydrogen.

---

[8] Storey, O. W., *Met. Chem. Eng.*, **14**, 683 (1916).

[9] Laissus, J., *Métaux*, **9**, 537 (1934).

[10] Laissus, J., *Chim. Ind.*, **29**, 515 (1933).

[11] Tsutomu Kase, (Abst.) *Metals and Alloys*, **7**, 454 (1936).

[12] Laissus, J., *Rev. Métall*, **32**, 293, 351, 401 (1935).

[13] Vawter, W. E., *J. Ind. Eng. Chem.*, **9**, 580 (1917); Haslam, R. T., and Carlsmith, L. E., *J. Ind. Eng. Chem.*, **16**, 1110 (1924); Guillet, L., *Compt. rend.*, **182**, 1588 (1926).

[14] Anon., *Mach.*, **42**, 540 (1936); *Ind. Bull.* (Arthur D. Little Co.) No. 112, p. 2, May, 1936.

Cemented or Sintered Carbide Coatings

Somewhat related to coating by cementation is the process of attaching sintered carbides to steel surfaces. The principal use of such coatings is for the production of cutting and grinding tools, although several localized wear and corrosion resistant applications have been suggested.[15] Carbides of tungsten, tantalum, titanium, etc. are prepared by heating intimate mixtures of the respective metal or oxide together with lampblack in a suitable atmosphere to temperatures ranging from 1500°-2400° C. The carbide thus formed is mixed with cobalt or nickel in the form of powder and heated until sintering. The carbides in a metallic binder of this kind, fashioned in suitable forms and shapes, are then brazed onto steel surfaces using copper, bronze or silver solders with suitable fluxes as the brazing media.

Mechanically Formed Coatings: "Metal-Cladding"

The veneering of base metal plate with noble metals has long been practiced, as previously mentioned. Just as the old process of making Sheffield plate depended upon the simultaneous rolling of silver and a copper-rich alloy, so also is the jeweller's gold-filled ware a gold or gold alloy shell filled with a base metal produced in a similar fashion. The commercial production of bi-metal strip, sheet or bars employing two base metals is of more recent origin. If a duplex ingot is made of two metals, that is, the central portion of one metal surrounded by a thick layer of the other, such as an iron or low-carbon steel center and copper covering, it is possible to roll the duplex ingot into the form of coated plate, bar or sheet; coated wire may also be drawn from the duplex billet. The finished product, in the example cited, has a coating of copper intimately alloyed to the steel base, the thickness of the coating being governed by the relative amounts of copper and steel in the ingot used and the amount of reduction received in working. Obviously the process is applicable only for those metals that do not differ radically in their rolling characteristics. The oxide film on alloy steels renders them difficult to bond to other metals by heating. In order to use them as a veneer for ordinary steel, their surfaces are electrolytically pickled in hydrochloric acid and electroplated with iron.[16]

Aluminum alloys are coated with commercially pure aluminum by casting an ingot of the alloy in a steel mold lined with sheet aluminum.[17] The aluminum coated aluminum alloy ingot thus produced is rolled to the desired dimensions without loss of continuity of the coating.

---

[15] For details of process and bibliography see MacKenzie, "Metals Handbook," Amer. Soc. Metals, 772, 1936.

[16] Grimshaw, L. C., *Trans. Am. Soc. Mining Eng.*, **120**, 363 (1936).

[17] Dix, E. H, U. S. Patent 1,865,089 (June 28, 1932).

It is reported that sheet zinc is successfully coated with aluminum by rolling sheets of zinc containing small amounts of aluminum together with aluminum sheets under pressure while hot.[18]

ELECTROPLATING

Electroplating is the most important method for the commercial production of protective metallic coatings with the possible exception of hot-dipping in the application of zinc and tin. Even in the case of zinc coatings recent advances have been mainly in the field of electrodeposition. Since the advent of chromium plating a few years ago there have been a number of new electroplating developments of promise such as heavy zinc coatings applied to wire, zinc, copper, nickel, and tin; brass coatings applied to steel strip; zinc and nickel coatings of markedly improved appearance; the electrodeposition of various alloys of controlled composition, etc.

Principles

The fundamental principles of the process of electroplating are familiar.[19] After a careful cleaning, the article to be plated is made the cathode of an electrolytic cell, *i.e.*, the plating bath, which is composed of a solution of the salt of the metal, the coating of which it is desired to electrodeposit. The anode of this cell is usually the metal which it is desired to electrodeposit but it may be another metal or some highly conducting material such as graphite which is insoluble in the plating bath under the conditions of operation. The plating operation is accomplished by passing a current through this cell, the source of electromotive force being a storage battery, a direct current generator or a rectified alternating current. Under the driving force of this applied potential, metal ions enter the solution by dissolution of the anode, and these ions and identical metal ions of the electrolyte move toward and reach the cathode and are there deposited in the metallic state. If the anode is of the insoluble type mentioned above the electrochemcial reaction at this electrode consists in the discharge of negative ions or anions and usually in oxygen evolution. In this case the metal ion content of the bath must be maintained by periodic additions of metal as oxide or hydroxide, thereby neutralizing at the same time the increasing acidity accompanying electrolysis under the circumstances.

According to Faraday's law the quantity of all of the elements liberated at either the anode or cathode during electrolysis is proportional to the quantity of electricity which passes through the solution. Since at the cathode hydrogen ions as well as metal ions may be discharged, the efficiency of the process of metal deposition may be, and usually is, less than 100 per cent. Similarly the dissolution efficiency of the anode may vary from the theoretical maximum to zero depending upon the proportion of the total current entering the solution by dissolution of metal. In certain plating baths anodes may undergo corrosion of the local action type, in which case the apparent anode efficiency may exceed 100 per cent. With any given plating conditions, the thickness of the deposit is proportional to the period of deposition.

---

[18] Kesper, J. F., *Tech. Blät, deut. Bergwerkzeit*, 23, 343 (1933).

[19] For a more complete discussion of the subject consult a text such as Blum and Hogaboom, "Principles of Electroplating and Electroforming," 2nd ed., New York, McGraw-Hill Book Co., 1930.

The successful operation of a plating bath requires the control of at least three variables, namely chemical composition of the plating solution, temperature of solution, and cathodic current density. These variables are related in their effect upon the character of the electrodeposit in such a way that if the range of one is changed it may be necessary to alter the others. Since it is usually desirable in commercial production to employ maximum current densities it is customary to adjust the bath composition, the temperature and other factors affecting the plating operation in such a way as to attain this end. Movement of the article being plated or movement of the plating solution with respect to this article generally permits the use of higher current densities.

Character of the Deposit

In actual practice, electroplating metal surfaces is not nearly as simple as might be inferred from the description given above. The character of the deposit, and hence its usefulness as a metallic coating, varies within very wide limits according to the plating conditions. First of all, the surface to be plated must be free from extraneous materials of all kinds. It is usually desirable that the deposited metal be distributed uniformly over the surface to be covered even though this surface be very irregular, as is often the case. In order to accomplish this purpose, solutions of rather complex composition are often employed. For example, alkaline cyanide solutions are particularly effective in depositing the required thicknesses of metal in recessed areas, thus exhibiting what is known as high "throwing-power." The use in certain baths of "addition agents" which often are of a colloidal nature is another method of obtaining this result. The deposits obtained by both of these means are usually smooth and fine grained in character. In the first case the fine grain structure results from the small, but constant, concentration of metal ions provided by dissociation of complex cyanide ions, while in the second case the restricted grain-size is due to the polarizing effect of the addition agent.

The deposition of coatings of uniform thickness is dependent also upon the proper arrangement and spacing of the parts to be plated with respect to the position of the anodes. The movement of the cathodes in the solution, as in "barrel" plating, aids in uniform distribution of deposited metal over the surface. Owing to the irregular shapes of many articles certain areas are generally nearer than other areas to the anodes and for this reason receive somewhat heavier deposits.

The importance of porosity of coatings depends upon the electrochemical relation of the coating metal to the base metal; if it is electronegative or anodic toward the base metal in the environment in which the article is to be used the existence of pores in the coating is not particularly disadvantageous, since under these circumstances the coating metal protects the underlying metal by sacrificing itself. If, on the other hand, the coating metal is electropositive or cathodic to the base, corrosion of the base metals will occur—the well recognized "pinhole" rusting. To illustrate, where iron is to be protected, coatings of zinc or cadmium may contain pores without seriously reducing their protective value, whereas if the coatings are of such metals as copper or nickel, continuity and freedom from pores are essential to prevent corrosion.

The formation of pores or pits in electrodeposits is generally associated with the adherence to the cathode surface either of gas bubbles, usually hydrogen, or of suspended particles of a miscellaneous character. The presence of metallic impurities of low hydrogen overvoltage in the base surface is conducive to hydrogen bubble formation, particularly in baths of high acidity.

It is essential that the metal be deposited in a dense, compact condition. Porous spongy deposits may occur owing to the formation of metal hydroxides and their codeposition with the metal. This is particularly true of relatively neutral solutions in which the film of solution adjacent to the cathode readily becomes alkaline as the evolution of hydrogen proceeds. If the solution is a dilute one and unagitated, so that the solution film adjacent to the cathode surface is depleted of metal ions, this tendency toward a spongy deposit is also pronounced.

The adhesion of electrodeposited coatings to the base metal depends primarily upon their intimate contact. The presence of grease, oxides or other extraneous materials markedly reduces adhesion. It is well known that a roughened surface, such as produced by sandblasting, improves the bond between coating and base probably by a mechanical keying action. Under suitable conditions the crystals of the deposited layer may be formed as direct extensions of the crystals in the base metal.[20] Such a coating becomes an integral part of the article. While instances of incipient diffusion of copper and gold coatings into zinc at ordinary temperatures have been observed, it may be said that, in general, electrodeposits do not alloy with the base metal unless subsequently heated.

METAL SPRAYING AND SPRAYED METAL COATINGS

Production of metallic coatings by spraying has attained commercial importance in the protection of metals from corrosion. Any metal available in the form of wire and fusible in the oxyhydrogen flame can now be sprayed on almost any surface. While the process is particularly suitable for the application of coatings to large structures, such as storage tanks and bridges, it is also used in the coating of small articles. In repair shops metal spraying is now commonly employed to build up worn or undersized parts. This application, as well as such miscellaneous uses as the metallization of non-metallic surfaces, is outside the scope of the present book.

---

[20] Blum, W., and Rawdon, H. S., *Trans. Am. Electrochem. Soc.*, **44**, 305 (1923); Graham, A. K., *Trans. Am. Electrochem. Soc.*, **44**, 427 (1923).

The metal-spraying process is associated with the name of the Swiss engineer, M. U. Schoop, who more than anyone else is responsible for its sucessful commercial development. The process is a special application of an older process of powdering metals. In 1882 a process of making lead powder by passing a stream of molten lead through a gaseous blast was patented in Germany. Somewhat later, mechanical methods of atomizing metals were developed in Switzerland and France. In principle these methods consisted in allowing molten metal to impinge upon rotating paddle-wheels. Schoop conceived the idea of preparing a metal coating by placing the article to be coated directly in the path of the atomized metal.[21] In experiments with lead bullets fired against a stone wall Schoop had observed that the flattened masses adhered to the wall and that upon overlapping the bullets appeared to be welded together. As early as 1902 a process for producing a metal coating by impacting metal dust upon a base by means of a blast of unheated gas was patented but never used commercially. Some years later Schoop devised a successful modification of this process by providing for the use of ignited gas.[22] It was the design of a nozzle permitting an annular blast which had encouraged the first commercial development of the metal-spraying process by Schoop and his associates about 1910. At this stage a stream of molten metal supplied from a reservoir was employed. This reservoir of molten metal with the auxiliary parts weighed over a ton and the dust-spraying apparatus weighed over a hundred pounds—serious handicaps to the commercial utilization of the process.

The use of metal in the form of wire for spraying had been proposed in 1905. Some years later a suitable apparatus known as a "pistol" was designed for this application.[23] Subsequent developments of spraying equipment have all utilized some form of portable pistol whether for powder, wire, or liquid metal. The modern wire pistol weighs between three and four pounds. In the operation of this, and of the powder pistol as well, melting of the metal is accomplished by the use of an oxyhydrogen or oxyacetylene flame. The electric arc has been utilized as the source of heat in some designs thus making the apparatus still more portable.[24]

Typical gas-fired pistols in common use are those shown in Figure 8. In such instruments the metal in the form of wire is advanced into the nozzle of the pistol at a constant rate such that the end of the wire is melted and atomized continuously. The size of wire used depends upon the metal to be sprayed, and the character of the deposit desired. In general, wires 0.125 inch in diameter may be used for heavy-duty spraying, while for ordinary deposits, wires from 0.08 to 0.03 inch in diameter (approximately

---

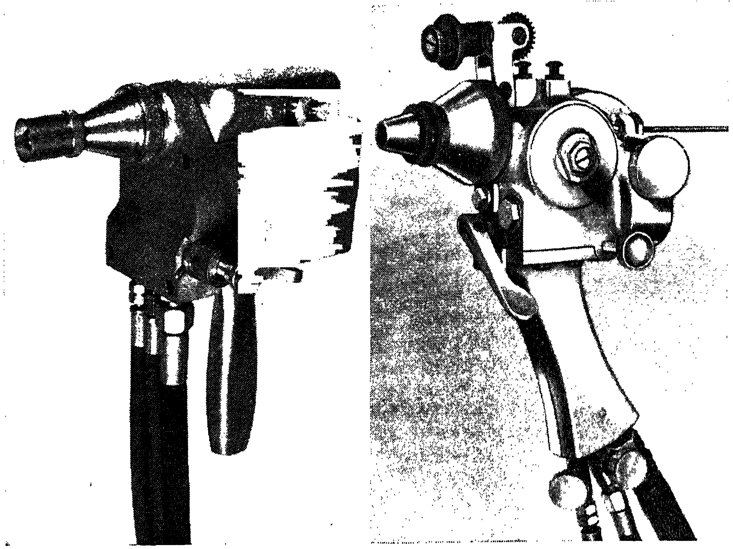
[21] Turner and Budgen, "Metal Spraying," p. 5, London, Chas. Griffen & Company, 1926.

[22] Schoop, M. U., U. S. Patent 1,128,059 (1915).

[23] Morf, U. S. Patent 1,100,602 (1914).

[24] Kasperowicz, W., *Zt. angew. Chem.*, **31 I**, 144 (1918); Gerber, F., *Die Metallbörse*, **23**, 510 (1933).

12 to 21 Brown and Sharpe gauge) are commonly used. The higher-melting metals spray more readily in the smaller wire sizes. These smaller sizes are used also where fine texture of deposit is desirable.



Courtesy of Metals Coating Co. of America, Metalspray Co., Inc.

Figure 8.—American Types of Gas-fired Metal Spray Pistols.

In its simplest form, the nozzle of the gas-fired pistol consists of three concentric tubes as shown diagrammatically in Figure 9. The wire to be sprayed is advanced through the central one; through the annular space surrounding this central tube, the gaseous mixture of either hydrogen or acetylene and oxygen is passed, which upon burning at the orifice melts the wire in the inner part of the conical flame. Through the second or outer annular spaces passes the compressed air or other gas which accomplishes the atomizing and spraying of the metal as it is melted. Acetylene and oxygen are used at pressures of 15 pounds per square inch and air at 50 to 60 pounds per square inch. From the standpoint of the energy consumed the process is inefficient, about 2 to 3 per cent of the heat of the flame being utilized in melting the metal.

The driving mechanism for feeding the wire is usually a small air turbine driven in some designs by the compressed air used for spraying the metal. Among other mechanical features which are of interest are modifications or extensions of the nozzle, and rotating nozzles to permit spraying inside of pipes or other rather inaccessible surfaces. (Gas jets may be attached to the pistol when it is desirable to heat the surface being sprayed.)

The electrically operated pistol differs considerably in construction and operation. Two wires are used which for a portion of their length conduct the current, and upon arcing at the ends produce the heat necessary for melting the metal. It is possible with this pistol to spray the higher-melting metals such as molybdenum and tungsten.

The powder process of metal spraying is limited commercially to metals of low melting point and in particular to zinc which can be obtained reasonably cheap in the form of powder as a by-product from zinc smelters. The pistol invented by Schori[25] for the powder process consists essentially of two injector arrangements, one a blow pipe and the other an aspirator. The finely divided metal is sucked from the powder chamber by the aspirator and heated as it passes through the flame of the blow pipe. The coating produced is essentially the same in character as that produced by the wire-pistol process.

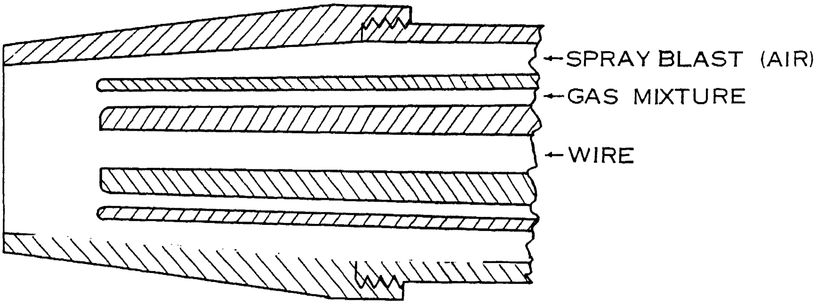


Figure 9.—Essential Features of the Nozzle of a Metal Spraying Pistol in which a Gas Flame is Used for Melting the Metal Wire.

In a later modification of the process of using liquid metal a pistol was developed by Jung in Holland to accommodate four pounds of metal previously melted in a gas-heated crucible. This process also is limited to low-melting metals, and the pistol is rather heavy. It is said to be rapid in operation and to produce coatings of uniform character.[26]

For coating small parts tumbling or revolving barrel machines have been devised, mainly abroad. Usually the articles to be sprayed are preheated in a separate compartment. The spray-guns are so arranged at the ends of the drum that the work is in the range of the spray during the tumbling operation. It requires from 10 to 20 minutes under these conditions to coat articles with zinc depending upon the thickness of coating desired.

The efficiency of deposition of sprayed metal coatings depends upon the process employed, the metal used and the distance of the nozzle from the surface being sprayed. For the wire pistol with the nozzle from 4 to 8 inches away the efficiencies of deposition are claimed to be as follows: Aluminum, 90-85%; high-carbon steel, 85-75%; brass, 80-75 %; zinc and tin, 73 to 67%; and lead, 65-60%.[27]

---

[25] British Patent 432,831.

[26] Lippert, T. W., *Iron Age*, 134, 8, Aug. 30 (1934).

Surface Preparation for Metal-Spraying

The most common method of preparing a surface for metal-spraying is that of sandblasting. Steel grit and cracked shot may be used instead of sand, and pickling in 4-per cent sulfuric acid is used to a limited extent where small articles are to be coated. It is desirable to apply spray coatings within a few hours after sandblasting in order to avoid superficial oxidation or contamination of the surface.

The adherence of sprayed coatings to the base is largely of a physical character, and depends upon roughening of the base surface. The sandblasting operation produces angular indentations and recesses which provide an improved anchorage for the coating. In contrast to electroplated coatings, which may under certain conditions continue the microstructure of the base metal, sprayed coatings are not so firmly bonded to the base metal. The strength of the bond in the latter case, however, is adequate for most practical purposes and has been shown to be as high as 700 pounds per square inch for coatings sprayed on properly sanded surfaces.[28]

The Nature of Sprayed-Metal Coatings

The fact that fine fabrics and other combustible materials may be metal-sprayed is astonishing at first acquaintance. If, however, a thermometer is placed in the range of the spray at a distance of 4 or 5 inches from the nozzle of the pistol it will be found that the temperature is but approximately 70° C. Evidently the metal in the wire process is melted, sprayed and again solidified at least superficially all in a small fraction of a second. Very likely the air film adhering to the surface of objects such as fabrics insulates them against heating until the deposited metal is cooled by the accompanying air blast. Schoop's original concept that fusion of the particles occurs at the instant of impact owing to the conversion of their kinetic energy into heat was later shown mathematically to be untenable.[29] A later microscopic study of metals sprayed upon glass indicated that the metal is either in a molten or plastic condition upon striking the surface to be sprayed and that a certain amount of spattering occurs upon impact. The powder process does not give the splash effect to such an extent as the wire process. Aluminum deposits made by this process have been found to consist almost entirely of rounded particles of metal each having a dendritic structure.[30]

---

[27] Tech. Bull. 106, Nov. 15, 1936, issued by Metals Coating Company of America, Philadelphia, Pa.

[28] Kunkler, L. E., *Mech. Eng.*, 58, 639 (1936).

[29] Arnold, H., *Zt. angew. Chem.*, 130, I, 209, 218 (1917); *Met. Ind., (London)*, 12, 121, 146, 165 (1917).

[30] Rollason, E. C., *J. Inst. Metals*, 60, 35 (1937).

It may be concluded from these observations that the particles upon striking the surface are flattened into relatively thin scales thus increasing the "covering power" of the metal. It is well known that these particles suffer superficial oxidation during the operation of spraying, in which compressed air is used. The characteristic stratification or lamination of sprayed metal deposits is apparently an oxidation effect. The undulating contours shown in the microstructure of cross-sections of sprayed coatings reveal the manner in which the deposits are built up from the component flattened and superficially oxidized metal particles. In spite of the oxidation effect, sprayed coatings made by the wire-pistol process have a high intrinsic tenacity.

As stated in the previous section, there is ordinarily no alloying action between the metal of the coating and that of the base metal. Similarly it has been shown that in coatings produced by spraying successively two different metals, for example, zinc and copper, no evidence of alloying of the two to form brass could be detected in the microstructure.[29] On the other hand, using an electric spray gun with a copper and a zinc wire [31] or spraying copper and zinc simultaneously [32] it is possible to produce deposits containing a certain amount of brass.

The density of sprayed metal is less than that of the same metal in cast form. In Table 2 is given a comparison of the values of density obtained for sprayed metals with the accepted values for the same metals in the ordinary form.

Table 2.—Density of Sprayed Metals Compared with the Density of the Metals in the Ordinary Form.

	Density of Sprayed Metal		Density (Int. Crit. Tab.) of Ordinary Metal
	Turner and Ballard [34]	Arnold [29]	
Aluminum	2.4	2.31	2.70
Zinc	6.4	6.32	7.14
Tin	7.1	6.82	7.31
Iron	6.5	...	7.86
Copper	8.0	7.51	8.92
Lead	...	9.77	11.34
Brass	...	7.32	8.30*
Bronze	...	7.77	8.76*

* Cast form of same alloys used for sprayed metal by Arnold.

This difference in density is to be attributed in part to oxidation and in part to the presence of pores and cavities. In the case of copper it has been shown [33] that the oxygen content of the coating may run from 0.3 to 1.25 per cent depending upon the design of the pistol, the oxygen pressure and distance of the nozzle from the surface to be sprayed. Porosity tests made upon similar copper deposits by immersion in a non-reacting oil *in*

---

[31] Schoop, M. U., and Kasperowicz, W., *Schweiz. Elektrotech. Zt.*, **16**, 33 (1919).

[32] Experiment carried out at Nat. Bur. of Standards and referred to by H. S. Rawdon, "Protective Metallic Coatings," p. 48, Chemical Catalog Company (Reinhold Publishing Corp.), 1928.

[33] Ballard, W. E., and Harris, D. E. W., *Met. Ind. (London)*, **49**, 482 (1936).

vacuo showed an absorption of oil comparable in its variation to the oxygen content. It is of interest to note that the porosity, as well as the oxygen content of the coating, may be reduced by using an inert gas instead of compressed air for spraying. By skillful manipulation of the air pressures in the ordinary method it has been found possible to spray coatings of lead, tin and zinc which are impervious to liquids.[34] Similar attempts to produce impervious coatings of copper, aluminum and brass were not successful.

The porosity of sprayed coatings may be reduced by mechanical treatment, as for example, hammering or wire brushing. Heating the article to be coated beforehand or spraying a thin coating of a low-melting metal, such as tin, and heating it to fusion before spraying the principal coating are other methods of overcoming porosity. Sprayed zinc coatings have the property of corroding in moist air to form corrosion products which fill the pores and improve the continuity of coating. The use of copal or Bakelite varnishes on sprayed nickel not only reduces the porosity of the coating, but appears to improve its adherence to the base metal.[35]

The particles of sprayed metals are, according to x-ray analysis, slightly work-hardened[36] and this together with the presence of oxide results in a hardness in excess of that of the same metal in the cast form. In Table 3 values are given for Brinell hardness of certain sprayed metals

Table 3.—Brinell Hardness Numbers of Deposits of Various Metals Made Under Different Conditions.

Metal or Alloy	Type of Pistol	Projecting Gas		Distance Projected (cms.)	Brinell Hardness of Deposit	Brinell Hardness of Large Mass of Metal or Alloy
			Pressure (kg/sq. cm.)			
Zn	wire	air	4	18	23	24
Zn	wire	air	4	18	23.5	24
Zn	powder	air	4	18	17.5	24
Zn	wire	N	4	18	19.	24
Zn	wire	N	4	5	18	24
Al	wire	air	4	18	35	21
Al	wire	N	4	18	35	21
Al	wire	air	2.5	18	28	21
Al	wire	N	2.5	18	32	21
Al	wire	air	4	5	40	21
Al	wire	N	4	5	36	21
Al	wire	air	2.5	5	26	21
Al	wire	N	2.5	5	30.5	21
Al	wire	air	4	18	84.5	50
Al	wire	N	4	18	90	50
Al	Spl. powder	air	4	18	102	50
Brass 70/30	wire	air	4	18	103	58
	wire	N	4	18	58	58
Mild Steel	wire	air	4	18	199	118
	wire	N	4	18	168	118
Stainless Steel 18/8	wire	air	4	18	187	160
	wire	N	4	18	106	160

---

[34] Turner, T. H., and Ballard, W. E., *J. Inst. Met.*, **32**, 291 (1924).

[35] Reininger, H., *Trans. Faraday Soc.*, **31**, 1268 (1935).

[36] Ballard, W. E., *Mech. World*, **97**, 103 (1935).

obtained in a recent investigation.[37] The coatings were 2 to 3 millimeters in thickness and the measurements were made with a ball 1.98 millimeters in diameter. The values given are the average result of three experiments.

In general, it will be seen that the sprayed metal is harder than the same metal in the ordinary form. It would appear from an inspection of these results that the deposits made with the nitrogen blast are lower in hardness than those in which the projecting gas is air.

The effectiveness of various sprayed metals in the protection of iron, steel and certain non-ferrous alloys against corrosion will be discussed in later chapters. It may be mentioned here that as compared with electroplated and hot-dipped coatings relatively greater thicknesses of sprayed metals are required to give the same measure of protection. For example, it is common practice for the protection of ferrous metals to use sprayed zinc and aluminum coatings 0.004 to 0.010 inch in thickness, depending upon the severity of the exposure. Similarly, tin and lead coatings run 0.010 to 0.020 inch in thickness and nickel coatings somewhat higher. In a comparison of the relative qualities of coatings sprayed by the wire and powder processes there was little difference observable for zinc (although the test had not been completed) but aluminum deposited by the wire method appeared to be superior.[30]

Practical Applications of Metal Spraying

Unlike most other types of metal coating, metal spraying may be readily applied to large and extensive metal surfaces *in situ.* Moreover the thickness of the coating can be controlled within rather narrow limits, and its composition can be varied. The coatings may be of commercially pure metals or of alloys such as Monel metal or brass, or they may be of two or more metals successively applied.

The foregoing features have led to the application of sprayed coatings to bridges, gas tanks, electrical transmission towers, hulls of ships, dock gates, the framework of street cars, tank cars, etc.

The small-scale applications of metal spraying are exceedingly varied and numerous, and no attempt will be made to list all of them. Certain structural parts of refrigerators, washing machines, furnace grates, condenser pipes, baffle plates, staybolts, screws and so on, have been successfully metal sprayed.

The use of metal spraying as a supplement to other coating processes is of interest. Sherardized coatings not infrequently show spots where the coating is either very thin or is lacking entirely. Such areas can be easily and quickly covered by metal spraying and rejections because of imperfect coatings can be almost entirely eliminated.

CATHODE SPUTTERING

When a relatively high voltage is applied between two electrodes in a partial vacuum inducing a glow discharge, it is found that the cathode undergoes disintegration and that the metal thus removed is deposited as a thin film on nearby objects within the tube. With a suitable design of tube or chamber it is possible so to arrange objects with respect to the cathode that their surfaces will be more or less uniformly metallized. This process, known as cathode sputtering, consists of three phases, namely, generation of metal gas, diffusion of gas, and condensation of gas in the form of a metal film.

---

[37] Fassbinder, J., and Soulary, P., *Met. Ind. (London),* **49,** 35 (1936).

It is well known [38] that the cathode metal is vaporized by local heating induced by positive ion bombardment. The potential required varies from 500 to 2000 volts depending upon the nature of the cathode metal. The greater part of the vapor thus produced condenses on the cathode itself, but a fraction of it diffuses throughout the tube and deposits as a sputtered film. The diffusion process is, of course, much influenced by the conditions of the vacuum, that is, the pressure, temperature and the nature of the other components present. While at lower pressures (10^{-4} millimeter of mercury) the atoms are diffused in a straight line, at the pressures existing in the sputtering chamber, 0.01 to 0.1 millimeter of mercury, the ordinary laws of diffusion prevail, with the result already described. The emitting cathode remains relatively cold during the process of sputtering as do other objects in the chamber on which the vapor condenses. Owing to this fact, it is possible to metallize paper, fabrics, waxes, etc., by this process.

The residual non-metallic gases in the sputtering chamber may influence the sputtering of certain metals. To avoid chemical reactions inert gases or hydrogen are generally employed. The rate of metal deposition is increased by sputtering in a heavy gas, being about fivefold more rapid in argon than in hydrogen.[39]

The metallic sublimate or deposit obtained in sputtering is crystalline in character and of a very fine-grained structure. It is assumed [40] that the metal is deposited in an amorphous state and that it subsequently crystallizes. There is evidence that the rate of crystallization is restrained by gases occluded in the deposit.[41] It is of interest that an increase in porosity of the film appears to be associated with crystallization. While thin films of sputtered metals may be highly porous, it is possible by increasing the thickness to about 0.001 millimeter to obtain deposits which are substantially pore-free.

Equipment and Methods of Operation

A sputtering chamber consists essentially in a vacuum-tight vessel fitted with a small anode, a large cathode and a fixture near the cathode for holding the object to be sputtered. The chamber is readily constructed

[38] Hippel, A. v., *Ann. Physik,* **81**, 1043 (1926).
[39] Cartwright, C. H., *Rev. Sci. Instruments,* 1, 758 (1930).
[40] Reinders, W., and Hamburger, L., *Ann. Physik,* **10**, 668 (1931).
[41] Joliot, F., *Ann. Physik,* **15**, 437 (1931).

from a bell jar fitted upon a heavy ground-glass plate. In certain commercial uses vacuum chambers of capacities up to six cubic meters are employed.[42] The anode may be located at a somewhat remote point in the chamber or even outside the chamber proper in a tube sealed into the vacuum line. It is customary to produce the necessary vacuum with a large capacity pump connected to the bell jar through a short length of large tubing. The vacuum system contains a McLeod gauge for reading pressures, and a bleeder valve. A constant pressure of residual gas may be maintained by operating the pump continuously and allowing air or inert gases to leak in slowly through the bleeder valve. Another method of operation consists in the use of a pressure regulating device which will stop and start the pump as required. It usually requires from 5 to 10 minutes to reduce the pressure of the system to the range 0.01 to 0.1 millimeter of mercury required for sputtering. The power may be satisfactorily supplied by means of a transformer which steps up the voltage from 110 to 10,000 volts using a rheostat in the primary winding for regulating the current.[43]

Commercial Applications of Sputtered Coatings

There are certain special applications in which cathode sputtering may be advantageously used for the production of metallic coatings. The process is particularly suitable for the metallization of electrically non-conducting materials, such as fabrics and phonographic recording waxes. The deposition of small amounts of silver in surgical gauzes by this means is said to provide materials of high oligodynamic action for the treatment of wounds.[44] In the metallization of sound recording waxes it is essential that the microscopic details of the surface receive a smooth continuous and adherent coating. This is faithfully accomplished by cathode sputtering with the production of a surface of improved quality for sound reproduction.[42]

Cathode sputtering has been successfully used in gold coating thin aluminum alloy diaphragms for carbon broadcasting transmitters.[43] It is necessary in this application that the gold coating be adherent, continuous and free from contaminating substances such as plating salts. Deposits of gold 0.001 millimeter in thickness produced by this method have proved superior in quality to electroplated gold coatings for this use. The aluminum alloy surface is suitably prepared for sputtering by scratch-brushing followed by rinsing first in acetone, then in ether, and finally by rubbing dry with filter paper.

COATINGS BY CONDENSATION OF METAL VAPOR

Closely related to cathode sputtering, but of more recent origin in practical application, is the production of metallic coatings by the condensation of metal vapors produced by thermal rather than electrical means. In this case the material to be evaporated is brought in contact with a heating coil or placed in a small electrically heated magnesia, alumina or graphite crucible which in turn is fitted into a coiled filament.[45] Tungsten and platinum wires are suitable for the heating elements. It is necessary to employ a higher vacuum in this process than in cathode sputtering. Pressures of 10^{-4} millimeter of mercury are satisfactory and must be maintained during the operation.

---

[42] Richter, K., *Koll. Zt.*, 61, 208 (1932).
[43] Fruth, H. F., *Physics*, 2, 280 (1932).
[44] Fischer, German patent application.

Metal deposition by this process is more rapid than by sputtering and it is possible to exercise better control of thickness. The temperature of the system must be maintained within certain limits. Should it become too high, the deposit becomes non-adherent and pulverulent owing to the fact that the metal gas density becomes so great as to cause condensation in the vapor phase.[42]

The following metals have been deposited by the thermal evaporation method: aluminum, antimony, beryllium, bismuth, calcium, chromium, cobalt, copper, gold, iron, lead, magnesium, manganese, nickel, selenium, silver, tellurium, tin and zinc. The method is generally not suitable for the deposition of alloys since there is a tendency in this case for the components to be fractionally distilled. While this process of producing metal coatings cannot be said to have attained commercial importance as yet, it shows considerable promise of special applications in the future.

---

[45] Cartwright, C. H., and Strong, J., *Rev. Sci. Instruments,* **2**, 189 (1931).

Chapter 4

Zinc Coating by the Hot-Dipping Process

The largest single use of zinc is in the form of zinc coatings. In 1934 over 42 per cent of the metallic zinc consumed in the United States was used for this purpose. This does not include the amount of this metal used as zinc dust, zinc oxide, lithopone and other zinc pigments in protective paint coatings. It is safe to say that fully half of the entire production of zinc is used for protecting other metals, notably iron and steel, against corrosion. The term "galvanized" as applied to zinc-coated iron had its origin in the concept of the "galvanic" (electrochemical) protection from corrosion afforded iron by contact with zinc.

It was in 1786 that Luigi Galvani, an Italian physiologist, described his classic observation that the suspension of frogs on an iron railing by copper hooks caused twitching in the muscles of their legs when the legs touched the railing—a reaction caused, as Volta later recognized, by the electric current generated by contact of dissimilar metals. "Galvanic action" thus came to arouse considerable interest and seems to have been recognized as a factor in the resistance of zinc-coated iron to corrosion.

Having been used since the early part of the 19th century the term "galvanized iron" has become rather firmly fixed commercially. In this book the word "galvanize" will be restricted to the process by which a zinc coating is produced by immersion in molten zinc, a process which might well be referred to as "zinc-dipping" in order to distinguish it from the other zinc-coating methods. The term "zinc-coated" will be used as descriptive of all articles coated with zinc irrespective of the process by which the coating may be applied.

HISTORY OF ZINC AND THE HOT-DIPPING PROCESS

It seems unlikely that the ancients had any acquaintance with zinc although a bracelet of silver inlaid with zinc has been reported from the ruins of Camiros which was destroyed in 500 B.C. Brass, however, was known in Biblical times. About 300 B.C. the Mossynoeci made brass by melting with copper a peculiar earth known as *calmia* which was found near the shores of the Black Sea.[1] The alchemists, notably Albertus Magnus, who lived in the 13th century, were familiar with the existence of zinc minerals which could be used to impart a golden color to copper. Zinc was not definitely recognized as a metal until Ebener in 1509 separated it from zinc slag or furnace calamine. Paracelsus (1493-1541) first referred to the metal using the term *Zinken.* The production of zinc by distillation from calamine was carried out by Kenkel in 1741 and by von Swab in 1742 and the production of the metal on a commercial scale was undertaken at Bristol in 1743.[2] There is considerable evidence that zinc was known and produced in the East long before it was in Europe. It is recorded that in 1745 an Englishman went to China to learn the process of zinç smelting. The Dutch in 1640 captured a Portugese ship laden with a cargo of zinc secured in the East.[3] The name "spailter" or "spiauter" used for the cargo is suggestive of the commercial term "spelter" still widely used for cast slab zinc.

---

[1] Rickard, T. A., *J. Inst. Metals*, 43, 297 (1930).

The first recorded experiments for producing zinc coatings by the dipping method are those of a French chemist, Melouin, in 1741. Tinned iron was already known at that time and Melouin attempted to zinc-coat iron sheets in a similar manner by immersion in a bath of molten zinc. The results of his experiments formed the basis of a report to the Académie Royale in 1742. Jean-Baptiste Kemerlin attempted to apply this process to coating kitchen utensils and the like in 1742, and by 1778 the use of zinc-coated iron utensils seems to have been fairly well known in parts of France.

In the description of the process given by Bishop Watson (*Chemical Essays,* 1786), sal ammoniac (ammonium chloride) was said to have been used.[4] There is evidence, however, that Bauschaendorf of Leipzig brought about the change from the use of a resinous flux to that of ammonium chloride. Bauschaendorf also recommended the use of a preliminary tin coating before immersion in the molten zinc, a practice which, although very early discarded, still survives in the usual dictionary definition of the process.

Sorel in 1836 was granted a French patent for a zinc-coating process which had practically all the essentials of the process as it is known today. The articles were to be cleaned in dilute sulfuric acid (9 per cent by volume), washed in water for 12 or 14 hours, then put in dilute hydrochloric acid and, after drying, immersed in a bath of molten zinc which was kept covered with a layer of ammonium chloride. On being removed from the zinc bath the articles were to be well shaken to remove excess metal and then plunged into cold water, after which they might be rubbed with sand and dried. The Sorel process was investigated by the French naval authorities and a very favorable report rendered concerning the protection from corrosion rendered to iron by this treatment. At nearly the same time, 1837, an English patent was granted to H. W. Crawford for a very similar zinc-coating process by hot-dipping which made use of ammonium chloride as a flux. A previous English patent granted in 1805 to Hobson, Sylvester, and Morehouse, which covered a method for coating iron with sheet zinc for the purpose of corrosion protection, may be cited as illustrating the importance attached to zinc as a protective metallic coating. The commercial development of the zinc-coating industry in England and in the United States is generally conceded to be the outgrowth of Crawford's patent rather than of Sorel's.

---

[2] Sang, A., *Rev. Métal.,* **9,** 1, 78, 160, 275, 343 (1912). This reference contains a rather complete historical development of the zinc coating process, and has been used freely in preparing the present account.

[3] Moulden, J. C., *J. Roy. Soc. Arts,* **64,** 495, 517 (1916).

[4] Trewin, C. S., *Bull. Am. Zinc Inst.,* **8,** 43, May (1925).

Coating wire with zinc was one of the first large-scale commercial applications of the zinc-coating process carried out mechanically. The coating of sheets was done entirely by hand in the early days of the industry. The patent of Morewood and Rogers in 1846 marks the first advance in the sheet-coating industry, in that mechanical regulation of the thickness and uniformity of the coating by means of rolls was attempted. They also recommended the use of an initial coating of tin to precede the zinc coating, as had Bauschaendorf previously. Experience showed, however, that the use of a preliminary tin layer was of no advantage and in fact was detrimental; therefore, it was gradually discontinued.

The success attained with the use of the coating machine for tin-plate, about 1863, stimulated action in the zinc-coating industry but, primarily on account of the very much larger sheets which had to be handled, it was not until a number of years later that a real solution of the problem was attained.

Outline of the Hot-Dipping Process

The hot-dipping process for covering metal products with metal coatings in theory is very simple. The article to be coated is properly cleaned and then completely immersed in the hot metal, and withdrawn with enough of the molten metal adhering as a surface film to give it the desired coat. In practice the process is not so simple, even with hand dipping. Preliminary cleaning of the metal products to be coated, fluxing of the surface of the bath of molten metal, regulation of the bath temperature and the use of addition agents in the metal are important factors, each of which has a bearing on the quality of the coating produced.

The dipping process as practiced for the production of zinc coatings is entirely manual for irregularly shaped articles such as structural parts, castings, bolts, nuts, nails and similar hardware, and such fabricated articles as ash cans, laundry tubs, vats, tanks and pails. Pipes are also, for the most part, dipped by hand. The dipping of materials of regular shape, *e.g.*, sheets, wire, woven wire fencing, etc., is done by means of machines, and involves larger tonnages than the hand-dipping process.

Preparation of the Base Surface

Cleaning the surface of the materials before coating is an essential operation, since the quality of the coating is markedly influenced by the character of this surface and its freedom from extraneous substances. There are two steps in the process of surface preparation following degreasing: the first consists of a pickling treatment in acid in which the oxide scale and inert material are removed from the metal; the second is a fluxing treatment, applied prior to submersion in the molten zinc bath, which serves to remove traces of oxides or iron salts. The iron surface prepared in this fashion is wettable by molten zinc. The same general method of surface preparation differing somewhat in details is used for wire, pipe, and other steel and iron products.

Pickling Treatment for Removal of Scale

The pickling bath used for removal of the scale layer from iron and steel is usually dilute sulfuric acid, although dilute hydrochloric acid is coming to be used more widely[5] and phosphoric acid to some extent for this purpose.[6]

In cleaning sheet stock the black sheets, suitably spaced in a basket of some alloy resistant to the action of the acid, such as aluminum bronze, are treated with dilute acid in a wooden tank or a steel tank lined with a rubber coating. The solution is kept warm either by coils of a lead pipe through which steam is passed or by jets of steam in the solution. The rate of pickling in sulfuric acid depends mainly upon the temperature of the bath and to a less extent upon the concentration of the acid. The best practice is to use from 4- to 8-per cent acid at a temperature not to exceed 80° C.[7] The average pickling conditions for sheets consist in the use of 7-per cent sulfuric acid at 60 to 95° C. and the time required under these conditions is 15 to 20 minutes.[8] When hydrochloric acid is used for pickling the rate of scale removal depends mainly upon acid concentration, and the operation is carried out at temperatures not exceeding 40° C. and usually in the range of 20 to 30° C. where the rate of pickling is comparable to that obtained with sulfuric acid under the average conditions given above. For cleaning castings, dilute hydrofluoric acid (approximately 5-per cent) is often used initially in order to dissolve grains of sand adhering to the surface. A surging of the solution up and down between the sheets is necessary as a mechanical aid in removal of the scale as it becomes loosened during the pickling operation. This is often accomplished by moving the sheets up and down in the solution. It is now known that the pickling acid loosens the scale by dissolving the underlying ferrous oxide layer of the scale which exists at the metal-metal oxide interface in the case of scales formed at higher temperatures.[9] It is of interest that scales formed at lower temperatures (below 575° C.) which should not contain appreciable amounts of ferrous oxide require longer periods for pickling. The mechanism of the acid attack on scale appears to be electrolytic in nature: the acid reaches the iron surface through pores in the scale and forms thereby electrolytic cells in which iron dissolves anodically and the scale (principally magnetic oxide with an outer skin of ferric oxide) being cathodic, is reduced to ferrous oxide which in turn is soluble in the acid.[10] The mean loss in weight resulting from the removal of the oxide scale from sheets is 150-300 grams per double-sided square meter of surface.[11]

---

[5] Bablik, H., *Iron Age,* **123,** 879 (1929).

[6] Hudson, J. C., *(Discussion) J. Iron Steel Inst.,* **126,** No. 2, 187 (1932).

[7] Imhoff, W. G., *Iron Age,* **126,** 82 (1930).

[8] Camp, J. M., and Francis, C. B., "The Making, Shaping and Treating of Steel," 4th ed., pp. 903, 968, Pittsburgh, Pa., Carnegie Steel Company (1925).

[9] Winterbottom, A. B., and Reed, J. P., *J. Iron Steel Inst.,* **126,** No. 2, 159 (1932).

It has become customary to use inhibitors in the pickling of iron in order to minimize the attack of the acid upon the metal surface. The development and general adoption of the modern inhibitor, together with improved pickling operations, have resulted in an overall reduction in acid consumption of 30-40 per cent.[12] Among substances which have been used more or less effectively as inhibitors in pickling baths are glue, gelatin, quinoline, pyridine, diethylamine, thiourea, sulfonated oils, etc. The use of such restrainers appears to be more necessary in sulfuric acid than in hydrochloric acid, where the rate of attack on the metal is low, particularly when it is used cold.[13] In the preparation of sheets for hot-dipping the use of minimum percentages of inhibitors has been found to prevent excessive liberation of hydrogen, which is sometimes conducive to blistering, without interfering with the slight roughening of the surface which is essential to the satisfactory adherence of the coating.[14]

It may be observed that these organic inhibitors are positively charged colloids or organic compounds which ionize readily. These substances become adsorbed on the cathodic areas of the iron as the scale is removed and restrain the discharge of hydrogen.[15] The resulting retardation of the acid attack upon the iron has been discussed in Chapter 1 and attributed to cathodic polarization. There is evidence that the inhibitive efficiency of certain organic compounds depends upon the structure and stereochemical arrangement of their positive ions.[16]

The pickling of iron and steel by electrolytic methods has been practiced to some extent. It has long been common practice to clean small parts by making them cathodic in warm alkalies. The Bullard-Dunn cathodic descaling process [17] makes use of an acid sulfate bath containing a small proportion of a metal salt such as stannous sulfate. As the scale is removed a thin deposit of tin is progressively formed over the cleaned areas and inhibits the solution of iron. More recently it has been proposed to descale iron by anodic pickling in dilute sulfuric acid or acidified ferrous sulfate solution.[18]

---

[10] Hoar, T. P., *(Discussion) J. Iron Steel Inst.*, **126**, No. 2, 191 (1932).

[11] Bablik, H., "Galvanizing," 2nd ed., London, E. & F. N. Spon, Ltd. (1936).

[12] Russel, P. R., *Am. Zinc Inst.*, 18th Annual Meeting (1936).

[13] Swinden, T., and Stevenson, W. W., *Fourth Report of Corrosion Comm. of Iron and Steel Inst. and British Iron and Steel Federation*, p. 185, (1936).

[14] Munger, H. P., *Trans. Electrochem. Soc.*, **69**, 85 (1936).

[15] Jimeno, E., Grifoll, I., and Morral, F. R., *Trans. Electrochem. Soc.*, **69**, 105 (1936).

[16] Mann, C. A., *Trans. Electrochem. Soc.*, **69**, 115 (1936).

[17] Fink, C. G., and Wilber, T. H., *Trans. Electrochem. Soc.*, **66**, 381 (1934).

[18] Müller, R., and Harant, L., *Trans. Electrochem. Soc.*, **69**, 145 (1936).

After sufficient pickling the sheets are washed with water, and are sometimes stored in a tank under water until ready to be coated. Immediately before coating the sheets are immersed for a few seconds in cold dilute (5- to 10-per cent) hydrochloric acid to remove the superficial rust which forms after pickling. In hand-dipping pieces of irregular shape the articles are thoroughly dried at this stage before being immersed in the metal bath. In the machine zinc-coating process some of the excess moisture is sometimes removed by rubber rolls before the sheets pass through the flux on their way to the molten zinc bath.

Fluxing Treatment

That portion of the surface of the metal bath through which the article is passed into the molten metal is kept covered with a flux which is commonly ammonium chloride, although zinc chloride or a mixture of the two may be used. There is, as a matter of fact, considerable variation both in the material used as the fluxing agent and in the manner in which it is applied. For example, a solution of ammonium chloride may be used together with hydrochloric acid, in place of hydrochloric acid alone, in the second stage of the pickling operation described in the last paragraph above. Another modification, the most modern practice, omits this step entirely and employs a solution of zinc and ammonium chlorides used in a ratio of one molecule of zinc chloride to three molecules of ammonium chloride.[19] Since the role of this bath is that of a deterrent to oxidation and a solvent for zinc oxide in or on the molten zinc, it is properly considered as a fluxing treatment. This solution containing from 5 to 20 per cent of the combined salts (depending upon the nature of the work to be fluxed) may be used either hot or cold.

The iron surface following the fluxing treatment is coated with a thin film containing ammonium chloride which, upon coming into contact with the molten zinc dissociates, yielding hydrochloric acid. This acid dissolves any oxide remaining on the iron surface and permits the zinc to wet the iron. It is of interest to mention that when an iron surface is cleaned by abrading with emery and then dipped in molten zinc no coating will form owing to the presence of an air-formed film of oxide.[20]

Other Methods of Surface Preparation

The oxide scale may be removed from iron by immersion in fused salts. Usually mixtures of sodium salts sometimes including caustic soda are used. It is claimed that a particularly effective means of cleaning telegraph wire consists in making the wire the cathode in a cell employing molten sodium hydroxide and sodium carbonate as the electrolyte.[21] Another pretreatment, an annealing step, sometimes used in the preparation of steel wire consists in passing it through molten lead prior to immersion in the zinc bath.[22]

---

[19] Baldwin, A. T., *Steel*, 99, 49 (1936).

[20] Daniels, E. J., *J. Inst. Metals*, 49, 169 (1932).

[21] Tainton, U. C., *Wire and Wire Prod.*, 9, 399 (1934).

Very recently it has been proposed to pretreat steel strip stock before immersion in the molten zinc bath by first heating the material in an oxidizing atmosphere at a temperature in the range from 170 to 500° C. (338 to 932° F.) to form a uniform oxide coating (appearing as a yellow to gray film) and subsequently reducing this thin oxide by passing the strip heated to the normalizing temperature (935-950° C.) through a reducing atmosphere, cooled to about 150° C. (302° F.) Finally the steel strip is passed into the zinc bath while still protected by the reducing atmosphere.[23] It is claimed that the film of reduced iron produced on the steel surface by this treatment improves the adhesion of the zinc coating and reduces its tendency to flake or chip off upon deformation.

The Molten Metal Bath

The ordinary bath used for coating steel sheets contains approximately 30 tons of molten zinc,[4] and "pots" containing as much as 75 tons are not uncommon.[8] The container used is either of open-hearth iron or a low-carbon steel plate, either riveted or welded together. Cast containers are used only for very small jobs. A coke fire was formerly used almost exclusively as the source of heat, but coal or oil has now, to a large extent, replaced it as a solid fuel, and natural gas is used considerably in this country. In the large installations the heat is transferred to the metal bath through the sides of the container rather than through the bottom. An electric furnace of the resistance type with a capacity of 8 tons of zinc has been developed for the zinc coating of small castings, pipes, etc.[24] In coating sheets and wire the machines for guiding the steel stock through the metal bath are placed partly beneath the surface of the molten zinc.

In many instances, a layer of lead 6 to 8 inches or more deep is used in the bottom of the zinc bath. The two metals, zinc and lead, are miscible only to a very slight extent. The main purpose served by the lead layer is to prevent overheating of the lower walls of the container, particularly when the pot is first started, and to reduce the attack of the zinc upon the hot walls of the container, thus adding to its life and also cutting down the amount of zinc-iron alloy, or dross, formed. It also serves as a cushion upon which the dross floats, which aids materially when the dross is removed. If lead is not added as such to the molten zinc, it is practically always present in appreciable quantity in the slab zinc used so that a lead layer gradually forms in the bottom of the pot.

Formation of Iron-Zinc Alloy or Dross

Upon immersion in molten zinc, a steel or iron article to be coated attains the temperature of the molten bath and is dissolved at its surface by the zinc. This alloying action between the two metals is an essential feature in the coating of metals by hot dipping. As will be shown later, the coating produced is far from being a simple layer of zinc but is rather complex and consists essentially of two rather sharply defined layers. The inner or alloy layer has a higher fusion point than the outer one, which is essentially zinc. The properties of the coating are very materially affected by this structural condition.

---

[22] Schueler, J. L., *Agr. Eng.*, 14, 339 (1933).

[23] Sendzimir, T., U. S. Patent 2,110,893 (March 15, 1938).

[24] Owen, S. Z., (Westinghouse Elec. Mfg. Co.) *Elec. J.*, 28, 631 (1931).

Naturally the walls of the container as well as all iron and steel parts immersed in the zinc bath are subject to attack by the molten zinc, so that the bath soon becomes saturated with iron. However, the principal source of iron in the zinc bath is from the decomposition of iron salts which may be carried over in the form of superficial films from the pickling or fluxing operations.[20] At 450° C. the saturation point or limit of solubility of iron in molten zinc is approximately 0.10 per cent of iron.[25] As the amount of iron in the zinc bath is increased beyond the solubility limit, crystals of the iron-zinc alloy, represented approximately by the formula $FeZn_7$ (10.9 per cent Fe), crystallize out of the molten metal and, being of slightly greater density than the zinc, slowly settle to the bottom of the zinc and float on the molten lead. The alloy-rich layer which forms is termed "dross."

The accumulation of the dross gradually interferes with the operation of the bath so that it has to be removed periodically, usually once a week. The material removed consists of a zinc-rich matrix, embedded in which are the crystals of the iron-zinc compound. The average iron content of the dross of "hard zinc" as it is often called is very considerably below that of the compound $FeZn_7$, since this compound in contact with zinc absorbs zinc without loss of its crystalline character until it becomes a solid solution. Analyses of plant dross generally show from 2 to 3 per cent iron.

The resistance of steel to the alloying action of molten zinc is but little affected by carbon contents up to 0.3 per cent; but above this and notably around 0.5 per cent carbon, the attack is markedly increased. Similarly the presence of 0.2 per cent silicon in iron results in a three-fold increase in rate of attack by molten zinc, whereas from 0.03 to 0.37 per cent manganese, 0.08 per cent sulfur, or 0.055 per cent phosphorus have practically no influence.[26] A phosphorus content of this order is considered by some to improve coating adherence.

The alloying action of molten zinc on iron is accentuated by an increase in temperature, particularly in the range above 500° C. Below this temperature it has been shown that the following relationship holds for the solvent action of high purity zinc on mild steel:[27]

$$L = n\sqrt{t}$$

---

[25] Peirce, W. M., *Trans. Am. Inst., Mining Met. Engrs.*, **68**, 767 (1923).
[26] Musatti, I., and La Falce, A., *Met. Ital.*, 28, 1 (1936).
[27] Daniels, E. J., *J. Inst. Metals*, **46**, 81 (1931).

where L is loss in weight of a unit area, n is a constant at a constant temperature, and t is time of immersion. Above 500° C. the relationship becomes

$$L = Nt$$

where N is a constant at a constant temperature and L and t have the same meaning as given above.

Thus it would appear that below 500° C. the rate of attack is determined by the rate of diffusion of zinc through a compact superficial layer of $FeZn_7$, but that above this temperature the alloy layer becomes porous and presents no impediment to attack. There is evidence that the change in character of the alloy layer occurs between 480 and 500° C. It is considered that a kettle should have a life of from 10 to 18 months if given proper care.[8] Calculations employing the equations given above indicate the following values for the life of a kettle with a wall thickness of 1.5 inches if used at the temperatures given:

At 432° C.	(810° F.)—	2410	years
477° C.	(890° F.)—	1487	years
500° C.	(932° F.)—	28	days
540° C.	(1004° F.)—	19.6	days

The average working temperature usually regarded as suitable in coating sheets is 450° C. and for zinc coating of wire from 445-465° C.[28] For large heavy objects in which the surface area is relatively small as compared to the mass of the body, bath temperatures as low as 425° C. are recommended in contrast to temperatures of 475° C. which might be suitable for small parts.[29] Since it is necessary in any case that the articles attain the temperature of the bath in order that adherent coatings may form, large pieces must remain in the zinc considerably longer than small ones. The tendency is for increased alloying action in the coatings as the period of immersion is increased, the temperature remaining constant, hence the reason for a somewhat lower coating temperature recommended for the heavier pieces.

At the exit end of the metal bath, a flux covering is not used, except in some very special cases. In the hand-dipping process, the surface is cleaned off with a wooden spatula just before the article is brought out. At the most, only very slight oxidation occurs which has no effect upon the weathering properties of the coating although it may alter the appearance somewhat. After hand-dipping, the coated article, such as a tub, is turned upside down to allow all excess zinc to drain off and may also be rapped sharply to aid in removing the excess zinc. Machines have been devised for removing the excess zinc from small articles, bolts, nuts, nails, small castings and the like by shaking or centrifuging, or by a combination of the two.

---

[28] Finkeldey, W. H., *(Discussion) Am. Electrochem. Soc.,* **47,** 201 (1925).
[29] Touceda, E., *Foundry,* **42,** 470 (1914).

Most zinc-coated wire, except that known as telegraph wire, is "wiped" as it emerges from the molten zinc to remove excess zinc and to give a smooth surface. The wiper may be a pad of asbestos which can be held on the opposite sides of the wire by suitable adjustable steel clamps. Telegraph wire is not wiped and hence has a somewhat rougher appearance than fence wire. In the latter case if the wiping is very severe only a very thin coating remains, which may consist almost entirely of the zinc-iron alloy layer. This is shown in Figure 10 which also shows the effect of bending upon coatings of this kind. The wiping of wires during galvanizing is not simply for the purpose of saving zinc, as is often supposed, but is often necessary to produce a coating which will withstand rather severe bending.

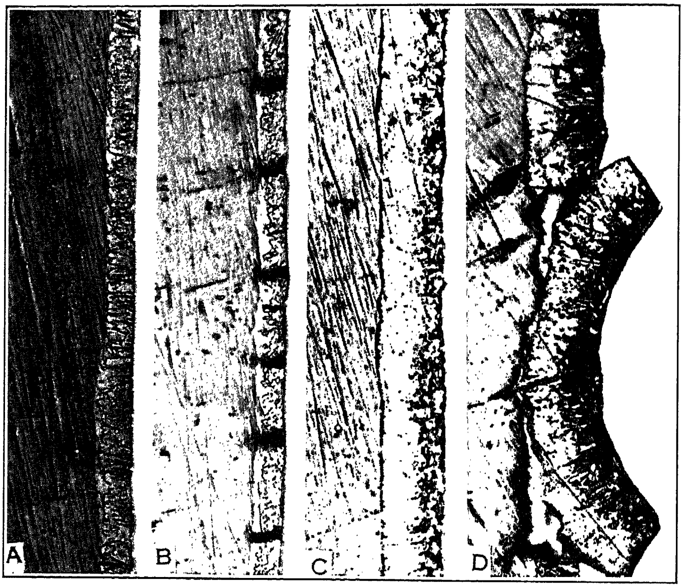


Figure 10.—Structure of Zinc Coating on "Wiped" Wire. ×350[30]

A. Tight Wiped Wire. All the coating except the alloy layer has been wiped off.
B. Same as "A" after the bend test in which it was wrapped around a wire of the same diameter.
C. "Asbestos-Wiped" Wire. This coating was not so closely wiped as in "A."
D. Same as "C" after the bend test of "B." The rough uneven surface of the alloy layer is largely responsible for the flaking upon bending.

For making wire with exceptionally heavy coating, the wiping may be done by drawing the wire vertically from the bath through a "header" of sand, charcoal or fine cinders. A hollow cone of zinc quickly freezes around the wire and functions as a wiper.

In coating sheets by machinery, the thickness of the coating can be regulated, at least approximately, by setting the exit rolls with respect to the surface of the zinc bath. By slightly changing the position of the rolls (often by adding more zinc to the bath), so as to increase the amount of zinc in the V-groove between the two rolls, a thicker coating is obtained, other conditions in operation remaining the same. The thickness of the coating on sheets varies somewhat from sheet to sheet and may vary rather widely on different portions of the same sheet. A variation of 17.5 per cent, that is, a variation of 0.35 ounce per square foot in a nominal coating of 2 ounces per square foot, is considered by many manufacturers [8] as good commercial practice even with present-day equipment.

Effect of Metallic Additions to Zinc Bath

It has been mentioned on a previous page that the presence of certain amounts of carbon and silicon in iron influences the rate at which it is attacked by molten zinc. In a similar way various metals when present in the zinc bath may affect both the rate of alloying with iron or steel and the character of the zinc coating so produced.

Aluminum.—The addition of 0.05 to 0.25 per cent aluminum (added in the form of a zinc-aluminum alloy) is widely used in the hand-dipping process for irregularly shaped articles. The greatly increased fluidity of the bath so produced is an advantage in affording greater penetration of the zinc into all crevices where in fabricated articles such as pails, dippers, tubs, etc., it must function as a solder as well as a protective coating. The use of aluminum is not generally favored in the coating of sheets in this country since it tends to produce dark spots on the surface. The presence of aluminum results in a decrease in the thickness of coating [11] and a marked reduction in thickness of the iron-zinc alloy layer [30] as shown in Figure 11. In appearance the coating assumes a relatively permanent bluish white lustre.

Tin.—It is customary to add tin to the zinc bath to improve the surface appearance and increase the uniformity and adherence of coating. While the use of tin in proportions as high as 3 per cent is reported, it is more common to employ less than 1 per cent. Tin produces large feather-like spangles white in color.[31] The effect of tin on the zinc-dipping process is, in all probability, to be ascribed to its influence on the melting point of zinc. The addition of even small percentages of tin causes the freezing of the metal to be spread over a considerable range of temperature, solidification not being complete until a temperature of 198° C. has been reached.

---

[30] Finkeldey, W. H., *Proc. Am. Soc. Testing Materials*, **26**, Part 2, 304 (1926).

[31] Brayton, G. A., *Address 18th Annual Meeting Am. Zinc. Inst.*, St. Louis, Mo., April 21, 1936.

Cadmium.—The presence of cadmium in excess of 0.05 per cent in the zinc bath increases its corrosive action toward iron and produces a coating of inferior bending qualities.[32] Cadmium does not of itself attack mild steel[33] but when present in the zinc bath it appears to render the $FeZn_7$ layer granular in character and thereby to obviate the restraining influence on the dissolution of iron otherwise exercised by the alloy layer.[20] Owing to this detrimental effect of cadmium it is desirable to avoid the use of cadmium-bearing zinc in the coating of telegraph and telephone wire, since such wire must be heavily coated and still be capable of withstanding severe deformation.[34] Very high-grade zinc has been used in coating the wire used in suspension bridges such as, for example, the Hudson river bridge at Bear Mountain, New York, and the Delaware river bridge at Philadelphia.[4] Cadmium is said to produce a silver fern-like spangle.

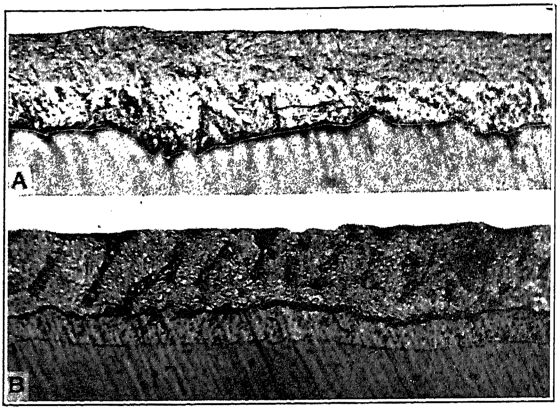


Figure 11.—Effect of Additions to Zinc Bath on Structure of Coatings. ×350[30]

A. The bath was treated with 0.2 per cent aluminum. Note the absence of alloy layers.
B. The bath was treated with tin. The oblique markings in the outer, or zinc-rich layer of the coating are the patches of tin-zinc eutectic.

Antimony.—The addition of antimony decreases the size of spangles in the coating even in the presence of considerable proportions of lead. In appearance the spangles assume a bluish lustre and have been described as "pearly"[35] and "ice-flowerlike."[36] Excessive percentages of antimony in the bath produce a yellowish stain in coatings.

---

[32] Bablik, H., *Metal Ind. (London)*, **37**, 411 (1930).

[33] de Lattre, G., *Rev. Métal*, **25**, 630 (1928).

[34] Ingalls, W. R., *Metal Ind. (New York)*, **14**, 429 (1916); Stone, G. C., *Iron Age*, **98**, 86 (1916).

[35] Imhoff, W. G., *Metal Cleaning Finishing*, **8**, 143 (1936).

[36] Arndt, L., *Z. Ges. Giessereipraxis*, **52**, 395 (1931).

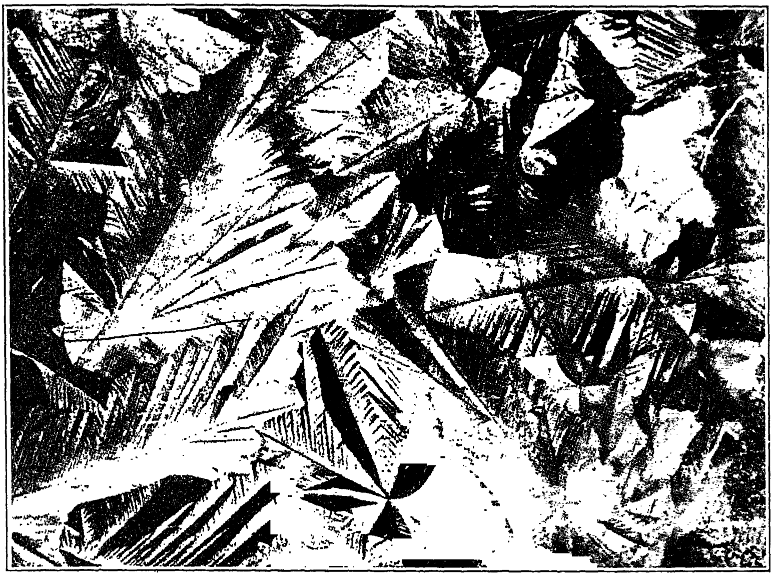


Figure 12.—Zinc-coated Sheet Showing Very Large "Spangles," Natural Size.[37]

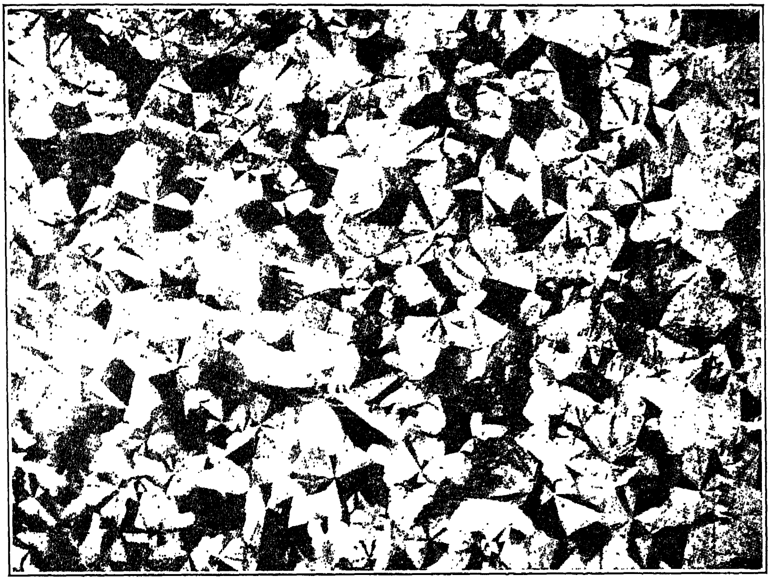


Figure 13.—Zinc-coated Sheet Showing Medium Size "Spangles," Natural Size.[37]

Other Factors which Affect Character of Zinc Coatings

The nature of the surface of the basis metal plays a part in determining the character and particularly the appearance of the zinc coating. The highest possible uniformity and cleanliness of sheet surface is essential for good coatings. Not infrequently the sheets after coating have a rough gray appearance, sometimes in certain portions only, and at other times over the entire surface. The beautiful fern-like pattern or spangle shown in Figures 12 and 13, which is regarded as desirable and is characteristic of high-grade material, may be entirely lacking on such sheets. This type of defect, the "gray sheet," illustrated in Figure 14, is often a cause of serious concern to sheet manufacturers. Although the character of the spangle is intimately related to the nature of the impurities in the zinc bath, as described in the preceding section, experience has shown that gray sheets may come from the same bath from which the majority of sheets coated at the same time are satisfactorily spangled. It is of interest that when representative gray sheets are stripped of their coatings by dilute acid and then passed through the galvanizing bath a second time, gray coatings are again obtained.[37] Similar results were obtained on sheets which were gray in certain restricted areas indicating that the location of the gray areas was

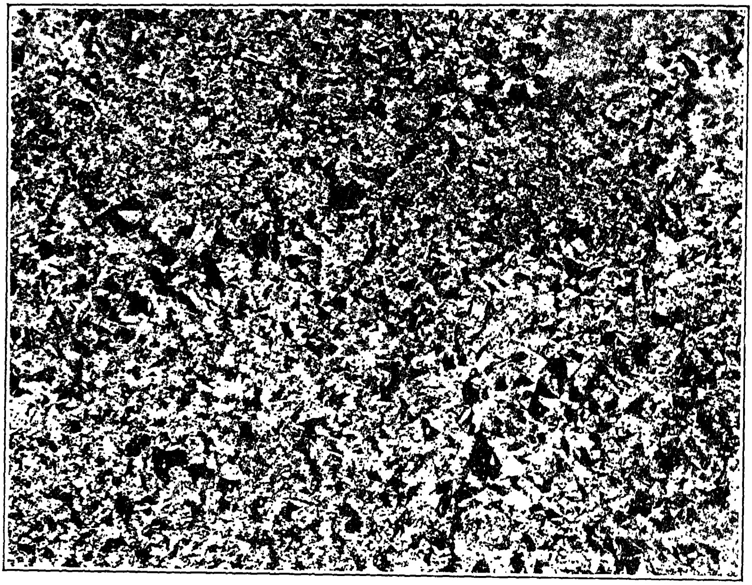


Figure 14.—Zinc-coated Sheet, Natural Size, Showing a Granular Dull Appearance Generally Known as "Gray Zinc."[37]

---

[37] White, G. A., *Iron Age*, 101, 934 (1918).

permanent. Coated wrought-iron sheets never have the beautiful spangled surface shown by coated steel sheets, their characteristic appearance resembling more that of gray sheet. However, if a wrought-iron surface is cleaned mechanically, that is, without pickling in acid, a marked change results and the spangle is often well developed.

There is evidence that one factor in the production of gray sheets is the retention of hydrogen by the iron during pickling. The surface of gray sheets from which the zinc has been removed has been found to be covered with blisters[37] which it is assumed were caused by hydrogen evolution upon contact of the steel with molten zinc. These blisters would be expected to provide numerous crystallization centers giving rise to the characteristic small crystalline coating. The inferiority of coatings on steel having pearlite along the grain boundaries has been attributed to the escape of hydrogen which had previously penetrated into the discontinuities in the grain structure of this steel.[38] In general, it may be said that any condition favoring a large number of nuclei for crystallization is conducive to the gray appearance.

Blisters in galvanized sheets are practically always associated with defects of the steel base rather than with the coating. On the whole, however, blistering is not a very common defect in zinc-coated steel sheets.

Adhering spots of the black or dark-colored flux which are sometimes termed "sally spots" in the mill, constitute one type of defect occasionally experienced. These are primarily defects in appearance only as it can be shown by removing the adhering deposit that the sheet is coated with zinc underneath the spots. Such spots are generally scraped off and the sheets passed through the zinc bath again. Incomplete removal of the oxide scale in the pickling operation usually results in bare or "black spots." Many such sheets can be reclaimed by scraping the spots free from scale, cleaning them with acid and recoating the sheet in the zinc bath.

Examination of galvanized sheets which have been slightly weathered often reveals many features which to one experienced in the manufacture of such material tell much concerning the preparation of the sheets. Lightly coated sheets often show transverse dark bands or "chatter marks" after weathering. The dark bands are generally considered to be somewhat of the nature of ripples in the alloy layer, the formation of which was caused by the "chattering" of the machine. There is no evidence to indicate, however, that chatter marks are to be considered as serious defects.

Very heavy zinc coatings do not completely solidify for several seconds after the sheet leaves the bath. It sometimes happens that the coating flows slightly on the sheet and causes a roughened, rippled surface. Such coatings are often referred to as "slipped coatings."

The contact of the links of the chain used for conveying the sheet away from the pot as it emerges from the bath usually causes early freezing of the zinc coating at these contact points. Large, well-developed rosette crystals or spangles form around these spots and thus record the position of the conveyer chain on the sheet.

---

[38] Schwarz, v., M., and Fromm, H., *Korrosion u. Metallschutz,* **11**, 241 (1935).

THE MICROSTRUCTURE OF IRON-ZINC ALLOYS

The pronounced solvent attack of molten zinc on iron or steel in contact with it has been repeatedly referred to in the foregoing discussion of the process of zinc coating by hot dipping. As a consequence of the alloying action between the two metals, the coating produced by hot dipping is far from being simply a layer of zinc spread over the surface of the steel. An iron content of only a few hundredths of a per cent is required to affect the structure of zinc to such an extent as to render the change detectable under a microscope. From microscopic and electrical conductivity studies the limit of solubility of iron in zinc at ordinary temperatures has been found to be 0.02 per cent.[25]

Inspection of the equilibrium diagram of the zinc-iron system of alloys indicates the existence of two intermetallic compounds of iron and zinc having the formulas $FeZn_7$ (10.9 per cent iron) and $FeZn_3$ (22.16 per cent iron). It is to the presence of these compounds, particularly the former, that the departure of a zinc-dipped coating from pure zinc, in structure and properties, is to be attributed in large measure. The entire time elapsing during the hot dipping of a sheet, for example, from the immersion of the sheet in the molten zinc until the adhering metal coating solidifies after leaving the bath, is very short, usually only a fraction of a minute. The speed of a sheet passing through the coating machine is from 40 to 70 feet per minute, according to the thickness of coating desired and the thickness of the sheet used. Hence, conditions of complete equilibrium such as are implied in the diagram do not obtain in practice. The alloying action is very rapid, however. It has been shown[39] that in galvanizing wire, if the iron wire is in contact with molten zinc for as short a period as one-twentieth of a second, an alloy layer can be detected in the microstructure of the coating.

The equilibrium diagram is very useful in indicating the trend of the changes which may occur, although perhaps not their true magnitude. The structure of zinc coatings which have been annealed after the coating operation (Figure 15) corresponds much better to the structure under equilibrium conditions, upon which the diagram is based, than do ordinary, unannealed coatings. An iron-zinc compound of formula $FeZn_{10}$ has been reported[40] but it is generally considered that the existence of this compound has not been definitely established.

EFFECT OF THE HOT-DIPPING PROCESS ON THE BASE METAL

The reported detrimental effects on the base metal caused by hot-dipping are more properly to be attributed to some of the incidentals of the process than to the effect of the molten zinc itself. It is a well established fact that brittleness can be induced in steel as a result of pickling in acid although the change, in general, is of a temporary nature.[41] It has also been claimed [42] that inferior tensile and torsional properties found in some wire coated with zinc by means of hot dipping were to be attributed to hydrogen retained by the metal. No well substantiated case of this kind has ever been reported, however. The greater part of the hydrogen in the steel to which the brittleness is usually attributed is driven off at a rather low

---

[39] Finkeldey, W. H., *Trans. Am. Soc. Testing Materials,* 26, Part 2, 304 (1926).

[40] Storey, O. W., *Met. Chem. Eng.,* 14, 683 (1916).

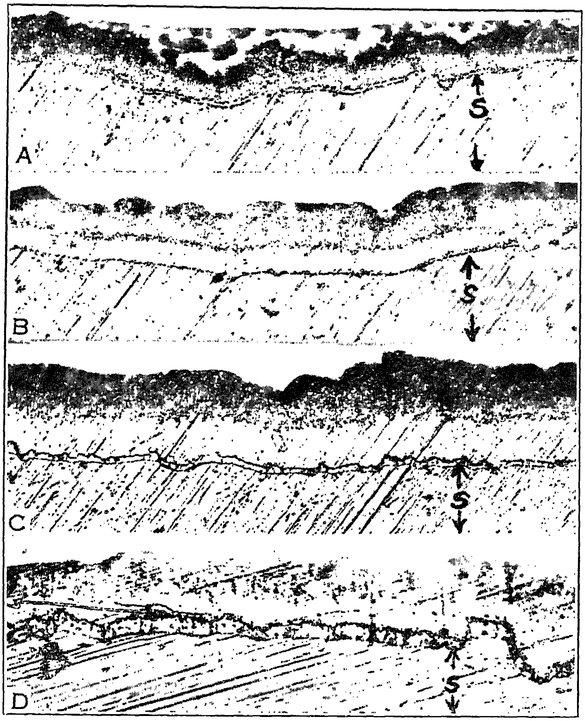


Figure 15.—Effect of Annealing Upon the Alloy Layers of a Zinc Coating. ×350[30]

A. Commercial hot-dipped zinc coating on an iron sheet which is indicated by weight of coating, 1.25 oz. per sq. ft.
B. Same after heating 2 hours at 350° C. Note prominence of the alloy layer.
C. Same as "A," after heating 4 hours at 350° C. Note how the thickness of the second alloy layer has increased.
D. Same as "A" after heating 5 hours at 350° C. The coating consists essentially in two alloy layers; the outer one corresponds rather closely to $FeZn_7$ in composition; the inner one, to $FeZn_3$.

---

[41] Langdon, S. C., and Grossman, M. A., *Trans. Am. Electrochem. Soc.*, **37**, 543 (1920); Polansky, V. S., *Forging—Stamping—Heat Treating*, **10**, 267, 298, 350 (1924); Edwards, C. A., *J. Iron Steel Inst.*, **110**, 9 (1924); Williams, R. S., and Homerberg, V. O., *Trans. Amer. Soc. Steel Treating*, **5**, 399 (1924); Alexejew, D., and Polukarow, M., *Z. Elektrochem.*, 32, 248 (1926).

[42] Winter, H., *Rev. Métal*, **7**, 1064 (1910).

temperature, approximately 200° C. (392° F.), so that it is extremely improbable that, at the temperatures employed in the hot-dipping process, an amount great enough to affect the mechanical properties of the metal would remain in the steel. The results given in Table 4[43] on samples of wire of the same reel are representative of the changes in the mechanical properties of the base metal which may be expected as a result of zinc dipping.

Table 4.—Strength of Wire Before and After Zinc-Coating.[43]

Electroplated[1]			Hot-dipped			No coating applied		
Spec. No.	Tensile Strength[2] (Kg./mm^2)	Elongation (%)	Spec. No.	Tensile Strength[2] (Kg./mm^2)	Elongation (%)	Spec.	Tensile Strength[2] (Kg./mm^2)	Elongation (%)
1	252	1.0	1	166	5.2	As received	199	2.6
2	249	0.9	2	168	5.8			
3	228	1.4	3	193	4.5	Tempered 300° C.	200	5.4
4	182	2.1	4	168	7.1			
5	201	1.3	5	140	6.4	Tempered 450° C.	131	3.6
6	207	1.6						
7	193	1.8						
8	198	3.0						
9	178	3.7						

[1] The electroplated wire was evidently tested soon after being plated.
[2] Conversion factor: for lbs. per sq. in., multiply by 1422.5.

Brittleness of malleable iron castings coated by zinc-dipping often causes a good deal of concern to manufacturers of such materials. It has been definitely shown, however,[44] that the heat-treatment effect incidental to the hot-dipping process, especially quenching the articles after they have been dipped, is responsible for the brittleness rather than any effect of the zinc *per se*. Certain features of the chemical composition of the malleable iron also seem to play an important part in rendering some irons more prone to brittleness than others. Studies have shown that the brittleness after galvanizing of cold-worked steel such as chain links, articles stamped out of sheet steel and structural steel angles is related to the extent of cold working and mechanical deformation rather than to hydrogen embrittlement.[45]

The annealing action of the molten metal bath, of course, cannot be avoided. Hence the hot-dipping process is not suitable for coating articles of which the properties would be seriously impaired by the hot metal, such as springs. The amount of such work is very limited and such parts are usually small and lend themselves to electroplating.

---

[43] Lange, W., *Z. Metallkunde,* **13,** 161 (1921).

[44] Bean, W. R., *Trans. Am. Inst. Mining Met. Engrs.,* **69,** 895 (1923); Marshall, L. H., *Bur. Standards Tech. Paper,* **245,** (1923).

[45] Allan, J. C., and Geruso, R. L., *Heat Treating Forging,* **16,** 70 (1930); Epstein, S., *Proc. Am. Soc. Testing Materials,* **32,** (Part 2) 293 (1932).

SURFACE APPEARANCE OF ZINC-COATED SHEETS AFTER STORAGE

The surface appearance of galvanized sheets after being stacked together either in transit or in storage for a considerable time, especially in very humid atmospheres and near the sea, is often spoiled by the formation of a white bloom which is distinctly different from flux spots or similar defects arising in the dipping process. Such materials are not infrequently rejected upon receipt of the shipment although there is nothing in the literature on this subject to indicate that in general the change is anything more than a slight surface corrosion of the zinc coating. The presence of lead in the zinc coating is considered by some to contribute to this behavior. It has been shown that the attack results from the development of oxygen concentration cells. In the inaccessible parts of the stack where the sheets are in intimate contact with one another, the oxygen concentration is less than in the more open parts. Hence, such portions of the metal surface are anodic with respect to those portions which have free access to the air. The zinc is corroded, therefore, as moisture condenses on the surface of the sheets, to form zinc hydroxide which constitutes the white bloom. Pronounced corrosion resulting in serious defects of the zinc coating from this cause is not common, however, unless the exposure conditions are very severe such as those reported by Argüelles[46] for stacks of galvanized sheets left exposed to the weather in the Philippines, in which case very severe corrosion resulted in the inner portions of the pack.

[46] Argüelles, A. S., *Philippine J. Sci.*, **11**, 177 (1916).

Chapter 5

Zinc Coating by Electroplating and Cementation

ELECTROPLATING

Electrodeposited zinc is one of the most widely used protective finishes for small articles. Coatings of this type are used also on metal screening, steel strip, pipe couplings, and wire. The application of electroplated zinc to sheet stock is, however, still very limited. A notable recent development has been the production of electrogalvanized round wire directly from the purified solutions of zinc-ore concentrates used in electrolytic zinc plants. An advantageous feature of this process lies in the heavier coatings which may be obtained. The process is being extended to sheet and strip stock up to 36 inches in width.[1] The demand for improved appearance in zinc coatings has led in another direction to the development of the so-called "bright" zinc coatings of such fine crystalline structure that light is reflected specularly from their surfaces. The metallic sheen of these coatings is quite unlike the diffuse gray appearance of the ordinary zinc electroplate.

Plating Baths

The electroplating of iron and steel with zinc for protection against corrosion was proposed in 1840.[2] An alkaline zinc cyanide plating bath was patented as early as 1855,[3] although baths of this type assumed little commercial importance until about 1916.[4] The first patent on zinc plating granted in this country was in 1862 [5] for a bath containing "sub" or "proto" sulfates and "sub"-acetates. The early commercial zinc plating was from acid sulfate or chloride baths and by 1900 the process was extensively used. At the present time the two principal types of baths used for zinc plating are the acid sulfate and alkaline cyanide solutions. The purified solutions of zinc concentrates used, as mentioned above, for wire plating, are essentially acid sulfate baths from which various metallic impurities have been removed.

It is owing to the high hydrogen overvoltage of zinc that it may be plated from acid solutions. Although satisfactory deposits may be obtained from neutral and even from ammoniacal sulfate baths[6] it is the general practice to maintain sulfate solutions slightly acid in order to obtain deposits free from basic salts.[7] At high acidities considerable hydrogen may be deposited, particularly if impurities of low hydrogen overvoltage are present, producing thereby pitted or spongy deposits. Furthermore the tendency of zinc anodes to corrode upon standing in sulfate solutions results in a gradual reduction of acidity. It is common practice therefore to regulate acidity in the range of pH from 3.5 to 4.5 by the use of "buffers" such as sodium acetate or aluminum chloride or sulfate.[4]

---

[1] Tainton, U. C., *Private Communication*, April 28, 1938.

[2] Sang, A., *Rev. Métal*, 9, 1, 78, 160, 275, 343 (1912).

[3] Watt, A., "Electroplating and electrorefining of metals," rev. by A. Philip., 2nd ed., New York, D. Van Nostrand Co., Inc., 1911.

[4] Thompson, M. R., *Trans. Am. Electrochem. Soc.*, **50**, 193 (1926).

[5] Besley, C., U. S. Patent 36750 (1862).

Zinc sulfate ($ZnSO_4 \cdot 7H_2O$) is usually employed for preparation of the sulfate plating baths. From 150 to 300 grams of this salt per liter (20 to 40 oz. per gal.) may be used. Ammonium or sodium chlorides or sulfates may be added to the bath to increase its conductance. In order to improve the throwing power of the bath and the appearance of deposits addition agents are generally added to sulfate solutions. Usually these are substances of organic nature such as glycerin, corn syrup, licorice, and starch, but aluminum sulfate[8] has been used.

Sulfate plating baths are usually operated at ordinary temperature, and at current densities from 1.5 to 3.0 amperes per sq. dm. (14 to 28 amperes per sq. ft.) It is claimed that current densities up to 33 amperes per square decimeter (300 amperes per sq. ft.) may be employed commercially provided zinc anodes containing mercury and aluminum are used.[9] In the Tainton process of wire plating, to be described later, current densities as high as 220 amperes per square decimeter (2000 amperes per sq. ft.) are employed.

Alkaline zinc cyanide baths possess much better throwing power than do acid sulfate baths[10] and are therefore preferable for plating irregular parts having recessed areas. The deposits are darker in color than those from sulfate solutions although it has been found that the use of small amounts of mercury in the bath and in the anodes produces brighter deposits. The use of mercury is also said to be an advantage in cyanide zinc baths to be used in plating cast iron.[7] Care, however, must be taken in the use of mercury in zinc baths for zinc deposits containing an excess of mercury have been observed to exude droplets of this metal from their surfaces in time.

Alkaline zinc cyanide baths are complex in nature and contain at least zincate $(ZnO_2)^{--}$ ions, zinc cyanide complex $[Zn(CN)_4]^{--}$ ions and of course zinc Zn^{++} ions. The solutions may be made up from zinc cyanide and sodium hydroxide or from zinc oxide and sodium cyanide. The desirable concentration of zinc (expressed in terms of $ZnCN_2$) is between 30 and 60 grams per liter (4 and 8 oz. per gal.) and it is essential to have present an excess of cyanide and hydroxide. Apparently the best results are obtained when the ratio of the normalities of the combined sodium cyanide and hydroxide to the normality of zinc cyanide is equal to about 2.[11]

---

[6] Rogers, R. R., and Bloom, E., *Trans. Electrochem. Soc.*, 67, 299 (1935).

[7] Blum, W., and Hogaboom, G. B., "Principles of electroplating and electroforming," 2nd ed., p. 322, New York, McGraw-Hill Book Co. (1930). This text, which contains an authoritative description of plating operations, bath formulas, etc., has been freely drawn upon in the preparation of the present material. For greater detail the reader is referred to this text.

[8] Frölich, P. K., *Trans. Am. Electrochem. Soc.*, 49, 395 (1926); Wasilewski, L., and Weber, A., *Przemysl. Chem.*, 17, 259 (1933).

[9] Graham, A. K., and Kolupaev, P. C., *Metals and Alloys*, 7, 14 (1936).

[10] Horsch, W. G., and Fuwa, T., *Trans. Am. Electrochem. Soc.*, 41, 363 (1922).

Alkaline zinc cyanide baths are usually operated in the temperature range of 40-50° C. (104-122° F.) and at current densities from 2 to 3 amperes per square decimeter (19 to 28 amperes per sq. ft.) More recently it has been shown that excellent deposits may be obtained from alkaline cyanide baths at current densities as high as 6.6 amperes per square decimeter (60 amperes per sq. ft.) using anodes containing aluminum and mercury.[12]

Anodes

Zinc anodes are cast or extruded from metal of high purity obtained either by electrolytic refining or by retort refining of ores which are free from objectionable impurities. The presence of copper, tin, antimony, arsenic, nickel, cobalt and lead is undesirable particularly in cyanide baths. The use of aluminum and mercury in anodes has been mentioned in the previous paragraph. Some years ago the use of 2 per cent of mercury in zinc anodes was proposed,[13] and later it was claimed that the addition of both mercury and aluminum (from 0.3 to 0.5 per cent mercury and 0.5 to 2 per cent aluminum) to zinc anodes is advantageous in the operation of both acid sulfate and alkaline cyanide zinc baths.[9]

Plating Tanks and Mechanical Equipment

Plating tanks are made of a variety of materials, the more common of which are steel lined with rubber and wood usually lined with lead, rubber, asphalt, tar pitch, sulfur-sand mixtures, etc. For acid sulfate solutions, lead linings are most commonly used although rubber-lined concrete is finding favor.[14] The tanks for alkaline cyanide solutions are generally of iron or steel construction used without linings.

Mechanical devices and automatic equipment for zinc electroplating have been developed to a very high degree of efficiency so that very little attention is required for their operation. The equipment varies according to the materials to be coated, but most of it is of one or the other of two general types, which may be designated as the "barrel" type and the "conveyor" type.

For zinc-plating bolts, nuts, screws, nails, washers, and in fact, all small articles which do not need to be handled individually in the plating bath, the barrel method, or a modification of it, is used. A perforated barrel made of some non-conducting material is immersed in the solution of the zinc salts, the electrolyte, and enough of the articles, properly cleaned, to fill the barrel partially, are placed within. They are in contact with flexible metal conductors on the inside of the barrel and together they form the cathode of the cell. The anodes, of cast zinc, are hung in the solution just outside the barrel and sometimes partially encircle it. The barrel is supported in the solution in such a manner that it can be rotated about its longitudinal axis. As the plating process proceeds the barrel is slowly rotated so that the articles are "tumbled" over one another, constantly exposing new surfaces to the plating current, thus ensuring a relatively uniform coating. In the conveyor type of equipment, the articles are moved through the plating solution past the anodes by means of an endless screw or a chain conveyor on which they are hung. The conveyor with the suspended articles upon it constitutes the cathode. Usually in this method the articles after having been attached to the conveyor are carried in turn through the preliminary cleaning and washing tanks, the plating tank and the final washing baths so that no handling is necessary except to place them on and remove them from the conveyor.

---

[11] Graham, A. K., *Trans. Electrochem. Soc.*, **63**, 121 (1933).

[12] Graham, A. K., *Trans. Electrochem. Soc.*, **67**, 269 (1935).

[13] Wernlund, C. J., *Trans. Am. Electrochem. Soc.*, **45**, 273 (1924).

[14] Stimmel, B. A., Hannay, W. H., and McBean, K. D., *Trans. Am. Inst. Mining Met. Engrs.*, **121**, 540 (1936)

For coating wire and wire products such as wire screen cloth, the process is also continuous. The wire passes in turn through the pickling and washing tanks, the plating bath and then through the final washing tank. As many as thirty wires, each from a separate reel, are passed through the bath simultaneously, and in order to permit the wire to be pulled through at a relatively rapid rate the plating tank must be made very long. For example, tanks as long as 150 feet are used for this purpose. Wire screen cloth is coated in an entirely analogous manner although it is often found advantageous to pass the screen up and down over a series of rollers to permit the use of smaller plating baths. In all the above cases, for any given set of plating conditions the thickness of the coating is determined by the length of time the articles are in the plating bath.

Electroplating of Wire

The zinc coating of round wire, telegraph wire, etc. by electroplating has received considerable impetus as a result of the improvements in the process made by U. C. Tainton.[15] Essentially the plating solution and the method of operation are those developed originally in connection with the electrorefining of zinc, but employing much higher current densities. Since 1933 this method has been in use for coating wire and a plant is now in operation rated at 250 tons of wire per day.[16] Whereas the weight of zinc coatings which can be applied to wire by the hot-dipping process

[15] Tainton, U. C., *Mining Eng. J.*, **126**, 856 (1928); Tainton, U. C., and Bosquin, *Trans. Electrochem. Soc.*, **57**, 341 (1930); Tainton, U. C., *Wire & Wire Products*, **11**, 225, 243 (1936); *J. Am. Zinc. Inst.*, **18**, 42 (1937); *Trans. Am. Inst. Mining Met. Engrs.*, **527** (1937).

[16] Cambria Plant of Bethlehem Steel Company at Johnstown, Pa.

seldom exceeds 1.2 ounces per square foot (0.002 inch in thickness) it is possible by the improved electrolytic process to obtain coatings of almost any desired thickness. Actually coatings of 0.8, 1.6 and 2.4 ounces per square foot are in commercial production.

The plating solution is derived from roasted zinc concentrates containing 50 to 60 per cent zinc and a wide variety of metallic impurities such as cadmium, copper, silver, lead, gold, iron, nickel, cobalt, manganese, aluminum, arsenic, antimony, silicon, calcium, magnesium, tellurium, etc.[17] These concentrates are dissolved in about 2 molar sulfuric acid,—usually the return-electrolyte from the cells following the removal of zinc which contains about 250 grams of sulfuric acid per liter,—and the impurities removed by various methods. The purified solution, as it goes into the plating cells, contains about 225 grams of zinc and from 200-270 grams of sulfuric acid per liter. The steel wire to be plated, after annealing by passing through a molten lead bath, is electrolytically cleaned in molten caustic soda and soda ash at 650° C. (1200° F.)[18] and then in acid solution. The electrodeposition of zinc is carried out at a temperature not to exceed 35° C. (95° F.) at current densities from 77 to 220 amperes per square decimeter (700 to 2000 amperes per sq. ft.) The anodes used in this process are lead containing 1 per cent of silver.[19] In one installation, a view of which is shown in Figure 16, plating cells are used which are 110 feet in length. There are in this case 12 wires in each cell and the wire speed through the bath is from 50 to 200 feet per minute depending upon the size of wire and thickness of coating desired. A heavy coating of froth is maintained on the surface of the bath to prevent excessive acid spray during the plating operation. The froth is obtained by the use of a small amount of a mixture of silicic and cresylic acids. Finally the plated wires are drawn through tungsten carbide dies for the purpose of smoothing and brightening the coatings.

Heavy coatings of zinc are being rapidly deposited on both wire and steel strip also from nearly neutral sulfate solutions containing a buffer and addition agents and using high-purity zinc anodes.[19a]

Excellent adhesion of the zinc coating is secured by this process. Coated wire, for example, can be drawn down almost indefinitely without any detachment of the zinc. A substantial tonnage of window screen is now made by coating No. 12 or No. 14 B & S gauge wire with four or five ounces of zinc per square foot, drawing this down to No. 31 or 32 gauge, and weaving it into screen.[20]

---

[17] Weisselberg, A., *Iron Age,* 137, 34, May 21 (1936); Tainton, U. C., *Iron Age,* 138, 59, Aug. 6 (1936); Anon., *Steel,* 98, 40, May 18 (1936).

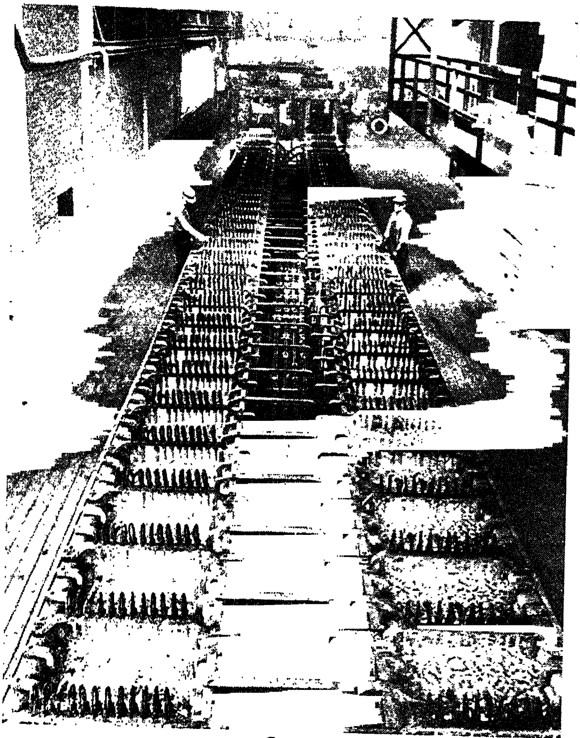
[18] Tainton, U. C., *Wire and Wire Prod.,* 9, 399 (1934).

[19] Tainton, U. C., British Patent 280,103, (April 29, 1927); Tainton, U. C., Taylor, A. G., and Ehrlinger, H. P., *Trans. Am. Inst. Mining Met. Engrs.,* 85, 192 (1929).

[19a] Lyons, E. H., *Iron Age,* Nov. 5, 1936; also Lyons, E. H., (Meaker Co.) *Private Communications,* Oct. 8, 15, 1938.

[20] Tainton, U. C., *Discussion, J. Am. Zinc. Inst.,* 18, 49 (1937).

This process is being applied on a pilot plant scale to sheet and strip stock up to 36 inches in width by the Bethlehem Steel Company at Sparrows Point, Maryland. It is expected that the results from the operation of the small plant will be used as a basis for the design of a commercial plant which will have in the first instance a capacity of about 100 tons of sheets per day.[1]



Courtesy American Zinc Institute.

Figure 16.—View of Electrolytic Cells in which Zinc is Plated on Wire. Each cell is 110 feet long and takes 40,000 amperes.[20]

"Bright" Zinc Electroplating

Within the past two or three years a number of processes have been patented for the production of bright zinc deposits. As mentioned previously the bright metallic lustre of these coatings is quite unlike the diffuse blue-gray appearance of ordinary electroplated zinc. As would be expected, the bright zinc deposits are but little affected by "finger-printing." However, it should be mentioned that in most exposures zinc corrodes at least superficially whether or not it is bright in the beginning. In other words, it has been observed that bright zinc tends in time to darken either uniformly over the surface or in localized areas.

Alkaline cyanide solutions form the basis of all the bright zinc plating baths. Addition agents in the form of organic compounds or soluble metal salts are employed in small proportions in all cases as a means of restricting the size of the crystals in the deposit. For example, there may be used for this purpose: methyl ethyl ketone; thiourea alone or with a salt of cobalt, iron or nickel;[21] thiourea with a salt of manganese or rhenium;[22] a reaction product of sulfuric acid and a terpene or terpene derivative;[23] or a flocculent colloidal substance, such as ferric hydroxide.[24] In the last-named case the bath is purified previously by the addition of a reducing agent, such as sodium bisulfite, sodium thiosulfate, phenyl hydrazine hydrosulfate, or formaldehyde, and the deposit obtained from the solution thus purified is said to be improved in ductility as well as in brightness.

The coatings obtained in the plating baths mentioned above are usually somewhat dull or brown in appearance and are finished by dipping in a brightening solution. A 1-per cent nitric acid solution may be employed for this purpose; but somewhat more satisfactory results may be obtained from a solution consisting of chromic acid to which small amounts of sodium sulfate and nitric acid [25] have been added.

Properties and Structure of Electroplated Zinc Coatings

An electroplated zinc coating is essentially pure zinc and, unlike coatings made by hot-dipping or cementation, contains no layers of alloyed iron. The average composition of such coatings is 99.85 to 99.90 per cent zinc,[26] and the product of the Tainton process is said to run 99.9975 per cent zinc. The nature of the impurities depends upon the composition of the anodes and the nature of the addition agents in the plating bath. Traces of lead, cadmium, copper and iron are likely to be the principal metallic impurities. Hydrogen to the extent of 0.055 per cent has been reported in freshly deposited coatings.[26]

Electroplated coatings will withstand severe bending or other mechanical deformation very much better than will other types of zinc coating of similar thickness. This is said to be particularly true of the high purity product applied to wire by the Tainton process and of the "bright" zinc coatings obtained at low current densities from highly purified cyanide baths.[24] Adherence tests made several years ago [27] in which the force required to separate the coating from the base metal was measured, showed the adherence of electroplated coatings to be nearly twice that of hot-dipped coatings. It is claimed that the adherence of plated coatings is materially increased by cathodic cleaning in fused caustic soda and soda ash.[28] The superior mechanical properties of zinc-plated coatings are, however, more properly to be attributed to the absence of the alloy layers than to greater adherence to the base metal. One interesting application of the improved mechanical properties of electroplated zinc coatings is the use of zinc-plated rivets for the fabrication of metal culverts and similar constructions. Even after the riveting operation, enough of the coating adheres to the head of the rivet to afford considerable protection against corrosion in service.

---

[21] Hull, R. O., U. S. Patent 2,080,483 (May 18, 1937).

[22] Hoff, E. F., U. S. Patent 2,080,479 (May 18, 1937).

[23] Pine, P. R., U. S. Patent 2,029,387 (Feb. 4, 1936).

[24] Oplinger, F. F., U. S. Patent 2,075,623 (March 30, 1937).

[25] Meyer, W. R., U. S. Patent 2,088,429 (July 27, 1937).

[26] Schwartz, v., M., *Z. Elektrochem.*, 29, 198 (1923).

[27] Burgess, C. F., *Electrochem. Metal. Ind.*, 3, 17 (1905).

The crystal size and form of electrodeposited zinc coatings vary within wide limits according to the conditions of deposition. With very low current density zinc will be deposited from either a sulfate or cyanide bath in the form of numerous isolated nodules rather than as a continuous layer.[4] At very high current densities pitting and rough deposits may result unless suitable precautions are taken for the elimination of impurities from the solution. Zinc coatings deposited from cyanide solutions have a very fine grain structure and a very smooth surface. The coatings obtained from sulfate baths, using addition agents, may approach those from cyanide baths in fineness of grain structure, and are much whiter and brighter in appearance. The ordinary deposits from both of these baths tend to darken in time and to finger-print. These disadvantages have been reduced in the so-called "bright" zinc deposits which are described on a previous page. Another method of preventing the finger-printing of zinc coatings which is practiced to some extent abroad, is the application of a clear lacquer to the freshly plated surface.

Zinc Coating By Cementation: "Sherardization"

Of somewhat less importance than hot-dipping and electroplating is the process of producing zinc coatings by cementation. The process is generally known commercially as "sherardizing," the term being derived from the name of the originator, Sherard Cowper Coles who discovered it about 1900.

It has already been pointed out that the alloying of metals by cementation was known many years before it was utilized commercially for the production of zinc coatings. The first patent for the production of metallic coatings by this means was issued a hundred years ago to Miles Berry, an Englishman, who proposed to protect iron from corrosion by coating it with copper.[29] While zinc may be applied by sherardization to copper and other non-ferrous metals the present discussion will be concerned only with the coating of iron and steel by this method.

---

[28] Tainton, U. C., *Wire and Wire Prod.*, 9, 399 (1934); Anon., *Steel*, 95, 22 (Dec. 24, 1934).

[29] Sang, A., *Electrochem. Met. Ind.*, 7, 485 (1909).

Outline of the Process

Sherardizing is particularly well suited as a process for zinc-coating small articles such as bolts, screws, nuts and small castings. It is not well adapted to sheets or wire, although the process in a modified form has been proposed for the zinc coating of wire.[30]

The articles to be coated, after cleaning, which as a rule need not be so drastic as for some other coating methods, are packed in zinc dust in a metal drum which may serve also as the shell of the furnace if the heating is to be carried out electrically. The container must be reasonably airtight and be equipped with a tightly fitting cover. The container together with its contents is heated either electrically by heating coils in its walls or by gas, and is slowly rotated during the heating. Care must be taken that the zinc-dust packing does not completely fill the container, so that as the drum is rotated a slight "rumbling" between the zinc dust and the articles to be coated may occur and intimate contact between the two may result. This feature of operation is important as the uniformity of the coating produced depends to a very large extent upon it. The character of the zinc dust used, particularly its iron content, and the temperature and period of heating, also have an important effect upon the coating produced. Fine zinc powder absorbs moisture rather readily, and on heating, hydrogen is said to be evolved.[31] The evolution of hydrogen by the heated powder is an advantage rather than otherwise as it reduces the chances for oxidation.

Commercial "blue dust," a by-product in the usual method for smelting zinc, is the material used generally, although a special form of zinc powdered to 200-mesh fineness is used to some extent in combination with the blue dust. The blue dust contains approximately 85 to 90 per cent metallic zinc, with 5 to 8 per cent of zinc oxide. In some of the earlier descriptions of the process it was proposed that inert materials, such as sand, be added to the zinc powder in order to prevent it from caking.[32] Apparently satisfactory coatings can be obtained using as high as 80 per cent quartz powder with zinc dust.[33] The addition of small percentages of naphthalene to the dust is said to prevent the formation of zinc carbonate.[34] The presence of iron powder lowers the rate at which the coating forms.[35] The practice of the most successful users of the process has not favored dilution of the zinc dust but rather the addition at intervals of small proportions of new dust to the used dust. The use of 10 per cent new dust and 90 per cent used material carefully freed from iron and oxide particles has been found to give excellent results.[36] Such a mixture of used and new dust has a metallic zinc content of 80 to 92 per cent.[37]

---

[30] Sang, A., *Trans. Am. Electrochem. Soc.*, **20**, 259 (1911); Bradley, A. F., U. S. Patent 2,009,573 (1935).

[31] Johnson, A. R., and Woolrich, W. R., *Trans. Am. Electrochem. Soc.*, **21**, 561 (1912).

[32] Sang, A., *Electrochem. Met. Ind.*, **5**, 187 (1907); Hinchley, J. W., *Trans. Far. Soc.*, **6**, 133 (1911).

[33] Kesper, J. F., *Oberflachentech.*, **10**, 108 (1933).

[34] Sauri, A. J., *Quim Ind.*, **7**, 117 (1930).

[35] McCulloch, L., *Trans. Am. Inst. Mining Met. Engrs.*, **68**, 757 (1923); Kuroda, M., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **16**, 125 (1931).

Effect of Temperature

The temperature at which the cementation process is carried out has a marked effect upon the rate of formation of sherardized coatings. This is shown in Figure 17 which compares the rate of coating of iron, nickel and copper by zinc cementation.[31] It will be observed that points are given somewhat beyond the melting point, (419° C.) of zinc. Presumably a film of oxide surrounding each dust particle prevents their coalescence to form a melt of any appreciable size. It is possible, therefore, for the

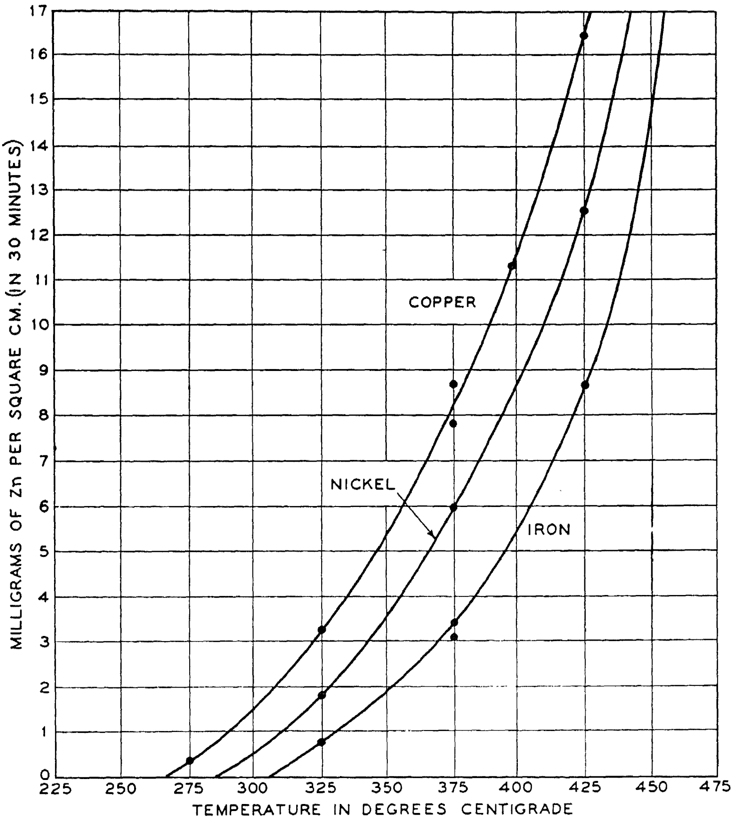


Figure 17.—Difference in the Rate of Coating Formation for Different Metals Heated in Zinc Dust.[31]

---

[36] *Iron Age*, **96**, 1108 (1915).

[37] Storey, O. W., *Met. Chem. Eng.*, **14**, 683 (1916).

cementation process to be carried out considerably above the melting point of zinc. The appearance and properties of the coating vary with the temperature used. For most purposes a rather low temperature is favored, and 350 to 375° C. has been recommended as desirable. For spring stock and tempered articles temperatures as low as 250° C. have been used, although the rate of zinc deposition at this temperature makes the process rather unattractive commercially. The rate of coating at 375° C. is such as to provide commercially a coating of 15 milligrams per square centimeter (0.5 ounce per square foot) in 2 to 3 hours. The thickness of such a coating is approximately 0.001 inch.

The iron content of the coating is affected by the temperature employed in sherardization. Coatings produced at relatively high temperatures have a considerably higher iron content than those produced at lower temperatures, other conditions of operation remaining the same. The temperature which it is necessary to employ depends also to some extent upon the composition of the dust used. For example, it has been reported [38] that with dust containing 7 per cent iron the temperature must be maintained at 450° C. (842° F.) in order to deposit a coating at the same rate that it is produced from pure zinc dust at 375°C. (707° F.) This also applies in the case of zinc-dross powder sometimes used in sherardizing.

The rate of zinc deposition is considerably reduced by the presence of a superficial film of oxide on the iron surface.[31]

Structure of Coating

The coating produced on iron by zinc cementation consists of fairly well defined layers if the outer rough portion of the coating, which appears to be built up mechanically, is disregarded. In coatings made at rather low temperature, for example, 350° C. or below, the greater part of the coating is a single-phase layer consisting of a solid solution of the compound $FeZn_7$ in zinc.[39] Although it is difficult to obtain a satisfactory chemical analysis of the coating at different depths below the outer surface, it has been observed in diffusion studies of the two metals that the average composition of the layer proceeding from zinc to iron ranges from 4.5 per cent iron to 17.7 per cent iron.[40] When iron foil is heated in zinc powder it has been shown that the minimum iron content of the product as a whole is approximately 6 per cent regardless of whether it was produced by heating at 365° C. for 2 days or at 415° C. for 45 days.[38] The average iron content of the principal layer of a sherardized coating runs usually from 8 to 10 per cent iron. Sometimes a second layer can be detected between the main layer of the coating and the iron base and, as the iron content of the coating is increased, generally as a result of a higher cementation temperature, this layer becomes more conspicuous. It is of a higher iron content and perhaps corresponds to the compound $FeZn_3$, indicated in the equilibrium diagram of the zinc-iron alloy system.

---

[38] McCulloch, L., *Trans. Am. Inst. Mining Met. Engrs.*, **68**, 757 (1923).

[39] Arnemann, P. T., *Metallurgie*, **7**, 201 (1910).

[40] Rigg, G., *J. Inst. Metals*, **54**, 183 (1934).

It is to be expected that, as either the temperature or the period of cementation is increased, the iron content of the principal, or outer, alloy layer will increase in accordance with the equilibrium diagram for the iron-zinc system of alloys. The formation of a well defined second (iron-rich) layer adjacent to the iron base is hardly to be expected until at least the inner portions of the first layer are fully saturated with iron. This would imply a composition corresponding to $FeZn_7$ in much of this layer.

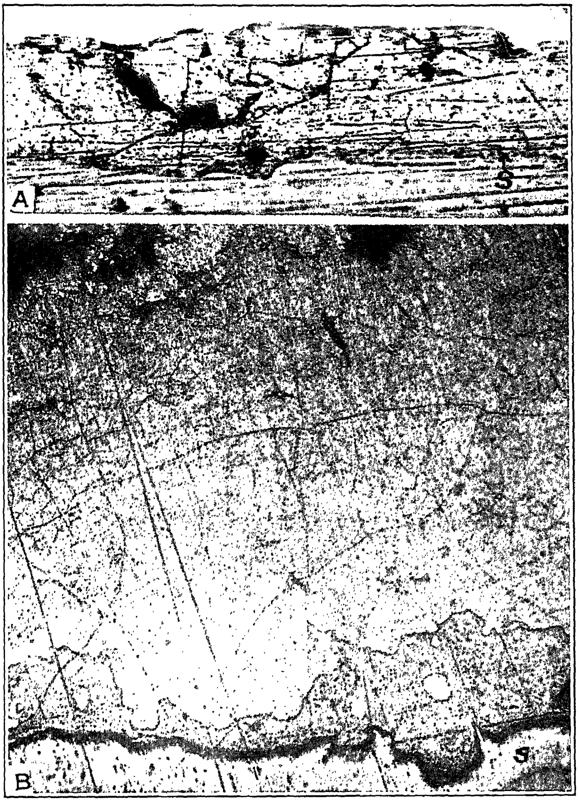


Figure 18.—Microstructure of Sherardized Zinc Coatings. [Rawdon, H. S., *Proc. Am. Soc. Testing Materials,* 18, pt. 2, 90 (1918).]

A. Cross-section of a Coating, 0.9 oz. per sq. ft., produced by sherardizing. S indicates the base metal. The fissured appearance is characteristic of coatings of this kind. The entire coating is made up of zinc-iron alloy. × 350.

B. Oblique section of a sherardized coating × 100. Note the two layers.

Figure 18 shows the microstructure of a sherardized coating. It will be noted that almost the entire coating is made up of one layer which has a characteristic fissured appearance. The outer part of this layer is rough and contains mechanically entrained inclusions, and on the inner side a very much thinner second layer exists.

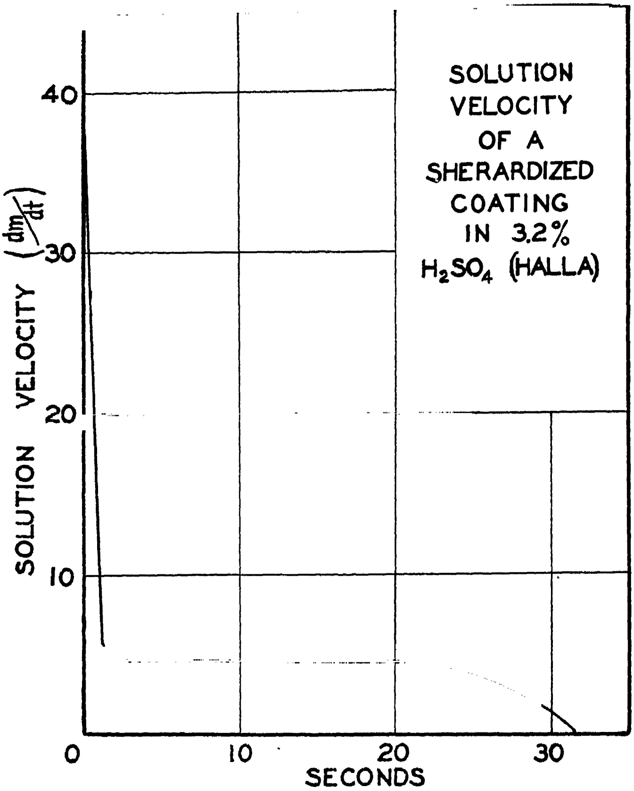


Figure 19.—Rate of Solution of a Sherardized Coating in Dilute Acid.[41]

Studies made of the "solution velocity" of sherardized coatings in dilute sulfuric acid confirm the conclusion based on examination of the microstructure that the bulk of any such coating is made up of a single and apparently uniform layer.[41] Nails sherardized under various conditions were used as material. Those used for the results in Figure 19 were heated for 3 hours at 365° C. in the zinc dust. From the loss-of-weight curves of the specimens immersed for given periods in the acid, the "solution velocity" was determined by graphical differentiation. It is seen that as the porous outer layer, high in entrained particles of zinc dust, is dissolved, the velocity of solution drops to a relatively low value and remains fairly constant for the rest of the coating, thus indicating uniformity of structure and composition for the coating as a whole.

---

[41] Halla, F., *Z. Elektrochem.*, **19**, 221 (1913).

Mechanism of Zinc Cementation Process

The zinc coating of iron by sherardization occurs by means of diffusion in the solid state. There has been difference of opinion as to whether the mechanism involves condensation of zinc vapor on the iron surface prior to the diffusion process or whether intimate contact of zinc powder and iron is essential. Solid zinc has a relatively high vapor pressure, approaching 0.1 mm. of mercury at 350-375° C., and it is conceivable that zinc may pass through the vapor phase in going from the dust particles to the iron surface. It has been observed[31] that with relatively coarse zinc dust (100- to 150-mesh) more rapid deposition of the zinc coating is obtained than when extremely fine dust is used. For example, at 370° C., without tumbling, a coating was built up by the coarser dust about twice as rapidly as with the fine material. The coating, however, was quite porous and lacked the uniform, smooth surface characteristic of those made by the use of the very fine dust. Recent diffusion studies[40] of solid zinc and iron in the temperature range 350-390° C., have shown that alloying proceeds only from the points of physical contact and furthermore that diffusion occurs mainly, at least, by a process of migration of iron into zinc.

Unsuccessful attempts have been made to develop a commercial method of zinc-coating based strictly upon the action of zinc vapor.[42] It would appear that both contact of zinc powder and iron and the presence of zinc vapor are essential to successful sherardization.

---

[42] Sang, A., *Proc. Engrs. Soc. West Penn.*, 23, 546 (1907); Cowper-Coles, S., *J. Soc. Chem. Ind.*, 28, 399 (1909).

Chapter 6

Protective Value of Zinc Coatings

NATURE OF PROTECTIVE ACTION OF ZINC COATINGS

Zinc is one of the more reactive metals. Free energy calculations show that it tends to corrode in the presence of moisture and air with the liberation of 71,500 calories for each gram atomic weight of metal converted into hydroxide.[1] Being readily corrodible zinc becomes coated with a film of corrosion products, the nature of which largely determines the eventual rate of corrosion. When a freshly prepared zinc surface is exposed to air of low or moderate humidities it combines directly with oxygen to form an oxide which is basally pseudomorphic with the underlying metal.[2] This densely packed oxide becomes converted after a few hours into the ordinary granular form of zinc oxide and from then on gain in weight with time follows a linear relationship.[3] That is, the rate of corrosion is determined by the rate of conversion of the pseudomorphic oxide into the normal zinc oxide,[4] the porous nature of the latter offering no impediment to the continuation of oxidation.

Under conditions of high humidity and atmospheric pollution the corrosion reactions of zinc become more complex and usually electrolytic in character. The corrosion products, formed when zinc was exposed in a Stevenson screen during the winter at the Royal Botanic Gardens, London, were found to be deliquescent at relative humidities of greater than about 75 per cent.[5] It is well known that such a deliquescent film accelerates corrosion by providing a moist conducting medium at the metal surface. At this location it was observed that zinc corroded nearly twelve times more rapidly in winter than in summer. In another test over a period of one year zinc exposed directly to the atmosphere corroded more than threefold more rapidly at Birmingham, an urban station, than at Cardington, a rural location.[5]

Rainfall removes about 75 per cent of the corrosion products from zinc surfaces if the results of tests in rural, urban and marine exposures are averaged together. The residual corrosion products remaining on the surface become basic in character and exert a retarding influence on corrosion. In highly industrialized or polluted atmospheres this basic film may not exist, a fact which may explain the more rapid attack experienced in such atmospheres.[6]

---

[1] Brown, R. H., Roetheli, B. E., and Forrest, H. O., *Ind. Eng. Chem.*, **23**, 350 (1931).

[2] Finch, G. I., and Quarrell, A. G., *Proc. Phy. Soc.*, **46**, 148 (1934).

[3] Vernon, W. H. J., *Trans. Faraday Soc.*, **23**, 135 (1927).

[4] Finch, G. I., *Discussion Trans. Faraday Soc.*, **31**, 1116 (1935).

[5] Hudson, J. C., *Trans. Faraday Soc.*, **25**, 207 (1929). A Stevenson screen is a wooden box with a double roof and louvered sides employed by meteorologists to shelter their recording instruments from rain and direct sunlight.

The actual rate of corrosion of metallic zinc in the atmosphere under normal conditions[7] is in spite of these implications so low as to be practically negligible. For example, if the rates of corrosion observed at Birmingham and Cardington, mentioned above, are maintained it may be calculated that the probable life of a sheet of zinc 0.030 inch in thickness such as might be used for roofing would be about 80 years in the former locality and 260 years in the latter.[5] This relative incorrodibility of so reactive a metal lies then in the protective nature of the film of zinc compounds which adheres to its surface. It will now be of interest to consider to what extent this inherent characteristic of zinc of forming protective films is a factor in the protective value of zinc coatings applied to ferrous metals.

It is obvious that so long as zinc forms a continuous envelope around the metal to be protected the coated article will display in a large measure the properties of zinc. Commercial metallic coatings are, however, seldom free from porosity and minor defects which expose the underlying metal. This is true for zinc coatings particularly in thicknesses of less than about 0.002 inch. In the zinc-iron galvanic couple arising from this porosity or discontinuity of coating, zinc is the anodic or corroding element, thus providing protection to the bare iron areas. Faraday discerned the sacrificial action of zinc in protecting iron when the two metals are in contact. His observation is recorded in his diary under date of November 26, 1829, as follows:[8]

"Clean iron nails laid on clean sheet zinc in dishes with fluid so that both iron and zinc partly in fluid, partly in air. For the purpose of observing the protecting power of zinc over iron. After many days examined. Where water the fluid, action and oxidation both of iron and zinc—no protection of iron—no serious corrosion of zinc by its contact. Apparently not more than where wood intervening. But where sol. of common salt used there iron fully protected; no corrosion of it, great corrosion of zinc—when wood intervening then both corroded. Hence zinc can protect iron and iron destroy zinc in this saline solution, but not in pure water. An evidence this of the effect of chemical action, etc. in exciting electricity. The iron nail on the zinc in solution of salt had much free alkali adhering to it."

It is apparent from these considerations that the effectiveness of zinc coatings in the protection of iron depends upon both the inherent resistance of zinc and its anodic electrochemical relation to iron. The influence of the environment upon the corrosion resistance of zinc has been referred to in a previous paragraph. Zinc coatings reflect to an even greater degree the acceleration of attack produced by polluted atmospheres. In the following table is given the calculated probable life of a zinc coating of 2 ounces per square foot of surface of steel exposed to the atmosphere in various localities.[9]

---

[6] Patterson, W. S., *Soc. Chem. Ind.*, 50, 120T (1931).

[7] That is, in the absence of factors conducive to pitting, such as contact with dissimilar metals or inert materials for periods of time.

[8] Faraday's Diary 1820-1862, Vol. 1, pp. 319-20.

Table 5.—Estimated Life in Years of a Galvanized Coating of 2 Oz. per Sq. Ft. of Surface (0.0033 in. thickness of coating) when Exposed to Atmospheric Corrosion.[9]

Locality	Type of Atmosphere	Approximate Life in Years
Overseas		
Khartoum	Dry tropical	150
Basrah	Dry inland	80
Apapa	Marine tropical	70
Singapore	Marine tropical	70
South Africa	Marine	20
England		
Cardington	Rural	25
Llanwyrtyd Wells	Rural	25
Bournville	Suburban	15
Wakefield	Industrial	10
Woolwich	Urban and industrial	20
Motherwell	Urban and industrial	15
Birmingham	Urban and industrial	8
Sheffield	Urban and industrial	5
Calshot	Marine	25
Southport	Marine	15
Doves Hole Tunnel	Railway tunnel	1

It will be observed that the highly polluted air of a railway tunnel is most destructive to a zinc coating which in country and seaside air protects iron for about 25 years. The attack in this case is electrolytic in character and the products of corrosion highly deliquescent. Absorption of sulfur dioxide as well as moisture by these products provides a medium of good electrolytic conductance at the metallic surface. Under these conditions electrolytic action would be expected to be rapid. This condition prevails to a lesser degree in urban and industrial localities where however rain tends to remove the greater part of the soluble products of corrosion which form in these atmospheres. In marine localities corrosion is also electrolytic in character but rate of attack is retarded by the protective nature of the basic corrosion products. At Khartoum and Basrah where conditions of low humidity prevail it seems probable that the mechanism of corrosion is of the direct oxidation type referred to in an earlier paragraph. Zinc coatings in the latter localities afford scarcely no electrochemical protection to iron. These atmospheres are not, however, very corrosive to iron.

---

[9] Fourth Report (Special Report No. 13) of the Corrosion Committee, Iron & Steel Institute, p. 12, London, 1936.

Performance of Zinc Coatings in the Atmosphere

Distinctive Properties of Various Types of Zinc Coatings

Previous chapters have contained accounts of the preparation and general nature of various types of zinc coatings. It will be of interest in the discussion of the corrosion behavior of these coatings to recall their distinctive characteristics and relative behavior. In order of the tonnage of zinc consumed in their production hot-dipped coatings stand first, followed by electroplated, sherardized and sprayed coatings.

The surface of zinc-dipped coatings, particularly sheet stock, is characterized by macroscopic crystals known as spangles. The demand which has grown up in the trade for a well-spangled sheet is based on the pleasing appearance rather than the superior quality of such sheets, for there is no good evidence that spangle is any indication of quality.[10] The results obtained with a certain accelerated corrosion test indicate that the outer or zinc-rich layer of the coating is relatively very thin along the margin of individual spangles when these are of large size.[11] The thickness of this outer zinc-rich portion of the coating depends upon the circumstances of manufacture and is usually less than that of the so-called alloy layer. It contains about 0.02 per cent iron in solid solution. It is largely the character of the alloy layer which determines the physical properties of the coating. This layer, as previously stated, is composed in the main of two intermetallic compounds $FeZn_7$, in the larger proportion, and $FeZn_3$ at the coating-iron interface. Both of these compounds are hard and brittle as compared with zinc, and the coating of which they form the major part will necessarily show these same properties to a considerable extent. For example, heavy coatings in which the alloy layers are well developed will, as a rule, flake readily from the iron base when the latter is severely bent. The outer surface of the alloy layer is said [12] to have a pronounced effect upon the brittleness of a hot-dipped coating as a whole, as exhibited upon bending. Coatings in which the crystalline form of the alloy layer is well developed and the contour of its surface irregular owing to fern-like growths prove, under test, to be much more brittle than coatings of similar weight in which the contour of the alloy layer is smoother and more regular. There is evidence [13] which indicates that the physical character of the alloy layer, as modified by annealing, may affect the behavior of the coating upon bending, as much as does the total amount of alloy present. A process [14] of heat treating zinc-dipped wire as it comes from the galvanizing bath, known as "galvannealing," is said to produce heavy coatings with good bending properties with no sacrifice in adherence. Upon deformation the stress in such coatings is probably relieved through the formation of numerous fine cracks. Cracking of a coating is not necessarily objectionable if peeling does not occur.[15]

---

[10] Camp, J. M., and Francis, C. B., "The making, shaping and treating of steel," 4th ed., pp. 903-13, 968-982, Carnegie Steel Company, Pittsburgh, Pa., 1925.

[11] Rawdon, H. S., Krynitsky, A. I., and Finkeldey, W. H., *Proc. Amer. Soc. Testing Materials*, 24, pt. 2, 717 (1924).

[12] Finkeldey, W. H., *Discussion Trans. Am. Electrochem. Soc.*, 47, 201 (1925).

[13] Finkeldey, W. H., *Proc. Am. Soc. Testing Materials*, 26, pt. 2, 304 (1926).

[14] Schueler, J. L., *Trans. Am. Electrochem. Soc.*, 47, 201 (1925); U. S. Patent 1,357,907.

Other factors affecting the ductility and adherence of zinc-dipped coatings are the purity of the zinc and the composition of the iron or steel base material.[15] "High Grade" zinc (containing less than 0.05 per cent lead and less than 0.01 per cent cadmium) is recognized as desirable for heavy-coated telephone and telegraph wire and for extra-heavy-coated sheets which are to be corrugated for such structures as highway culverts. Iron or low-carbon steel wire cannot without difficulty be coated with heavy ductile and adherent coatings. Steel wire stock of approximately 0.6 per cent carbon or rephosphorized steel of medium carbon content are suitable for the production of satisfactory zinc-dipped coatings.

Since much of the advantage of zinc as a protective coating depends upon its anodic nature with respect to iron, it is of interest to know to what extent this relationship is affected by exposure of the alloy layer as the outer zinc-rich portion of the coating is removed in the process of corrosion. Potential measurements show that the iron-zinc alloys which comprise this layer are anodic to iron, but by a lesser amount than is zinc in ordinary aqueous solutions. That is to say, these alloys protect iron, but under given conditions a lesser area of exposed iron will be protected from rusting. The inherent resistance of the alloy layer itself is comparable to that of zinc, so that in general the probable life of the coating is equivalent to that of an alloy-free zinc coating of the same thickness.

An electroplated zinc coating is essentially pure zinc. It may contain traces of copper, lead, cadmium and iron together with some inclusions, the nature of which depends upon the addition agents in the plating bath and the composition of the anodes. Hydrogen to the extent of 0.055 per cent has been reported in freshly deposited coatings.[16] In contrast to dipped coatings the structure of electroplated zinc is homogeneous, there being no alloy layer present. The crystal size and form may vary within wide limits according to the composition of the plating bath and the conditions of deposition.

Electroplated coatings will usually withstand mechanical deformation very much better than will other types of zinc coatings of the same thickness. In a certain type of adherence test[17] electroplated coatings were found to adhere with nearly twice the tenacity shown by zinc coatings made by the dipping process.

Cementation, or sherardized coating, consists essentially of a zinc-iron alloy of indeterminate composition, which, as would be expected, provides electrochemical protection to the iron base. It corresponds rather closely in composition and properties to the alloy layers of the zinc-dipped coating. As weathering occurs the coating gradually assumes a dark appearance, becoming finally a very dark gray if the iron content of the coating is not too high. Coatings high in iron usually show a red dusty surface upon weathering owing to the formation of ferric oxide. This reddish cast or stain sometimes creates the impression that the coating has been entirely corroded away exposing the ferrous base. It can be shown readily that such is not the case. There is evidence,[18] however, that such coatings are less resistant to atmospheric attack than those of lower iron content which form smooth black oxide finish upon weathering. That is, coatings containing about 15 per cent iron are appreciably less resistant to corrosion than those containing 11 per cent or less.[19] This difference in service life is to be attributed largely to the difference in the nature of the iron oxide film formed in the two cases rather than the relative electrochemical nature of the two. In the case of coatings low in iron, a closely adhering protective layer of iron oxide is formed, whereas the corrosion of the higher-iron layer results in loosely adhering flocculent rust which affords little if any protection to the metal beneath.

---

[15] Finkeldey, W. H., *Met. and Alloys*, 2, 266 (1931).

[16] Schwartz, v., M., *Zt. Elektrochem.*, 29, 198 (1923).

[17] Burgess, C. F., *Electrochem. Met. Ind.*, 3, 17 (1905).

If the zinc dust used in cementation is high in iron, particles of this metal may be mechanically enclosed in the outer layer of the coating with the result that the coating will become rust-stained upon weathering.

Sprayed zinc coatings, like other metallic coatings applied by this process, consist in an aggregation of minute particles somewhat flattened and superficially oxidized. The coating as a whole is generally somewhat stratified, owing possibly to the repeated passing of the spray over the surface as the coating is built up. In spite of this, it possesses a high degree of coherence although it is less dense than electroplated coatings. There is no alloying with the base metal and the adherence of the coating is of a rather low order. Although the coating is somewhat porous in character, there are usually no pinholes extending through it to the base.

Comparative Life of Different Types of Zinc Finishes

Numerous laboratory tests to determine the relative protection afforded by different types of zinc coating have been based generally upon the resistance of such coatings to attack by acids, or salt solutions or else the development of pinhole rusting in distilled water. The principal value of such tests has been the information obtained concerning the uniformity of coatings in thickness. The early conclusions of these studies that electroplated zinc coatings are markedly superior to other types in corrosion resistance have not been borne out by atmospheric exposure tests.

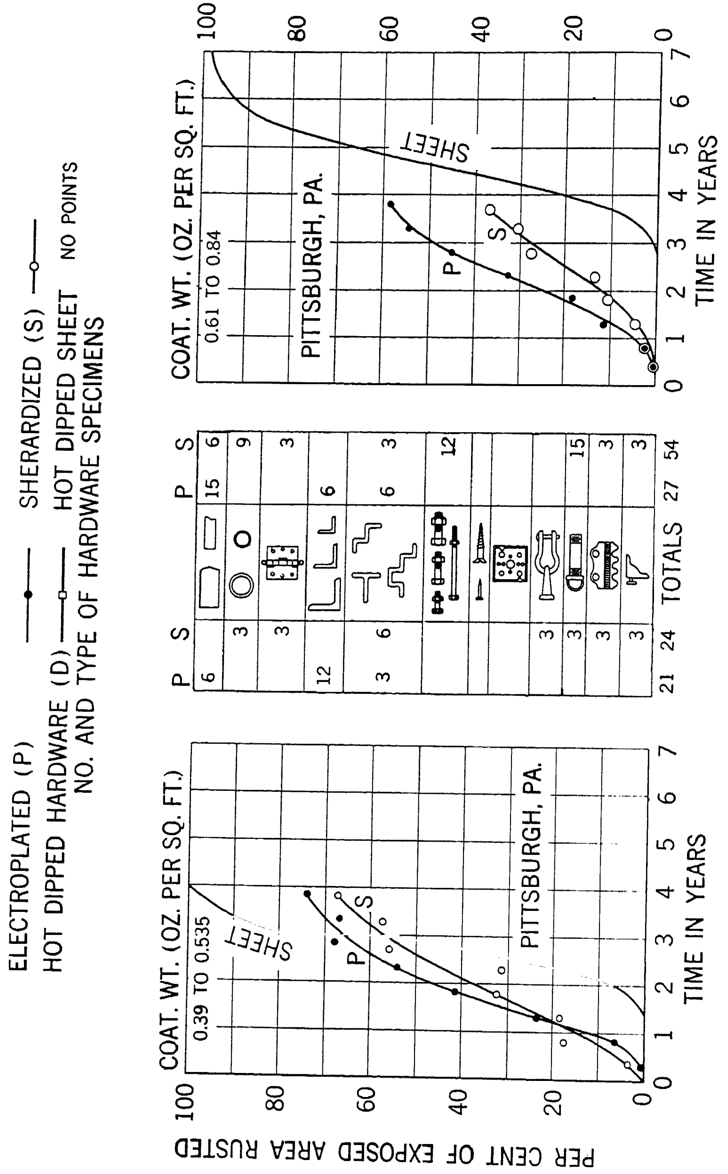
The most comprehensive outdoor atmospheric corrosion test on zinc coatings is that carried out by the American Society for Testing Materials.[20]

---

[18] Storey, O. W., *Met. Chem. Eng.*, **14**, 683 (1916).

[19] McCulloch, L., *Trans. Am. Inst. Mining Met. Eng.*, **68**, 757 (1922).

[20] For a full description of these tests see Reports of Subcommittee VIII, Committee A-5, on Field Tests of Metallic Coatings, *Proc. Am. Soc. Testing Materials*, **27**, (Part 1), 191, (1927); **29**, (Part 1), 149, (1929); **31**, (Part 1), 184 (1931); **33**, (Part 1), 156 (1933).


ELECTROPLATED (P)
SHERARDIZED (S)
HOT DIPPED HARDWARE (D)
HOT DIPPED SHEET
NO POINTS
NO. AND TYPE OF HARDWARE SPECIMENS
COAT. WT. (OZ. PER SQ. FT.)
0.39 TO 0.535
PITTSBURGH, PA.
SHEET
P
S
PER CENT OF EXPOSED AREA RUSTED
100
80
60
40
20
0
TIME IN YEARS
0
1
2
3
4
5
6
7
P S
6
3
3
12
3 6
3
3
3
3
21 24
TOTALS
P S
15 6
9
3
6
6 3
12
15
3
3
27 54
COAT. WT. (OZ. PER SQ. FT.)
0.61 TO 0.84
PITTSBURGH, PA.
SHEET
P
S
100
80
60
40
20
0
TIME IN YEARS
0
1
2
3
4
5
6
7

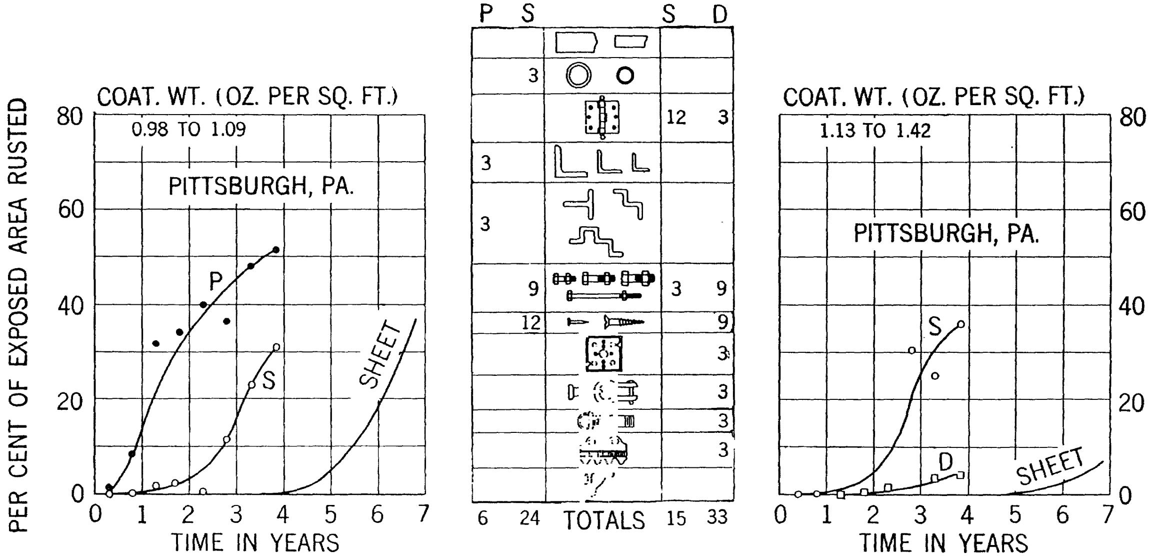


Figure 20.—Comparative Life of Zinc Finishes. (Pittsburgh Tests.) Hot-Dipped Sheet Coatings and Three Types of Zinc Coatings on Hardware.[21]

This general test of metallic coatings, which is still in progress, consists in the exposure of about 950 zinc-coated specimens on racks in the following five localities: Pittsburgh, Pa., Altoona, Pa., State College, Pa., Sandy Hook, N. J., and Key West, Fla. The first two locations are industrial in character; the third is rural, the fourth marine and industrial and the last, tropical marine. An analysis of the results of these tests after about six years of exposure has led to the conclusion that zinc-dipped, electroplated and sherardized coatings are "capable of being equally good in preventing rusting of the underlying iron provided adequate uniformity of coating is attained." [21] In Figure 20 the comparative life of hot-dipped sheet coatings, and hot-dipped, electroplated, and sherardized hardware are shown. The number and various shapes of the hardware articles are also represented.

It is apparent from an inspection of these results that uniformity of coating thickness is the principal factor in determining the relative life of different type coatings of a given thickness. As would be expected sheet stock upon which greater uniformity can be obtained gave the best performance, and electroplated hardware, where the distribution of coating in recessed areas is more difficult, made the poorest showing. Both plated and sherardized parts appear to be definitely inferior to those which were hot-dipped. Since the uniformity of coating should be somewhat similar for hot-dipped and sherardized coatings the results indicate that the sherardizing process is less effective than that of the hot-dipping process in the protection of iron. This confirms experience over a period of years in which it was found that malleable iron castings with sherardized coatings were less resistant to atmospheric corrosion than were similar castings with hot-dipped coatings.[22] It should be pointed out, however, that this experienced superiority of hot-dipped coatings is not reflected in the roof exposure test results obtained in New York City and shown in Figure 22.

In a corrosion test in which hot-dipped and electroplated specimens were exposed to the winter atmosphere in London [23] it has been reported that the former were the more resistant owing presumably to the formation of a less soluble, and therefore more protective, film of corrosion products. The total corrosion of the zinc-dipped coating at the end of 150 days was 2.97 milligrams per square inch and that of the electroplated coating 5.14 milligrams for the same area. However, in an exposure of about 180 weeks in the industrial atmospheres of New York and Pittsburgh it has been found that hot-dipped and plated zinc coatings of the same thickness furnish about the same protection.[24] It is understood that recent unpublished results from tests at Sandy Hook, N. J., and Washington, D. C., show

---

[21] Hocker, C. D., Symp. Outdoor Weathering of Metals and Metallic Coatings, *Am. Soc. Testing Materials*, page 1, 1934.

[22] Wolf, F. L., *Met. and Alloys*, **2**, 341 (1931).

[23] Patterson, W. S., *J. Soc. Chem. Ind.*, **47**, 313T (1928).

[24] Blum, W., Strausser, P. W. C., and Brenner, A., *Bur. Standards J. Research*, **16**, 185 (1936)

0.001 in. of electroplated zinc to be superior to the same thickness of hot-dipped zinc at those locations.

A more detailed comparison[21] of the effect of specimen shape on the life of plated zinc is shown in Figure 21 where the results of electroplated angle and flat shapes separately are compared with hot-dipped sheets. The angle parts failed in the shortest time, and the flat parts in most cases are somewhat less durable than sheet stock.

INDIAN INSTITUTE OF SCIENCE
LIBRARY
BANGALORE

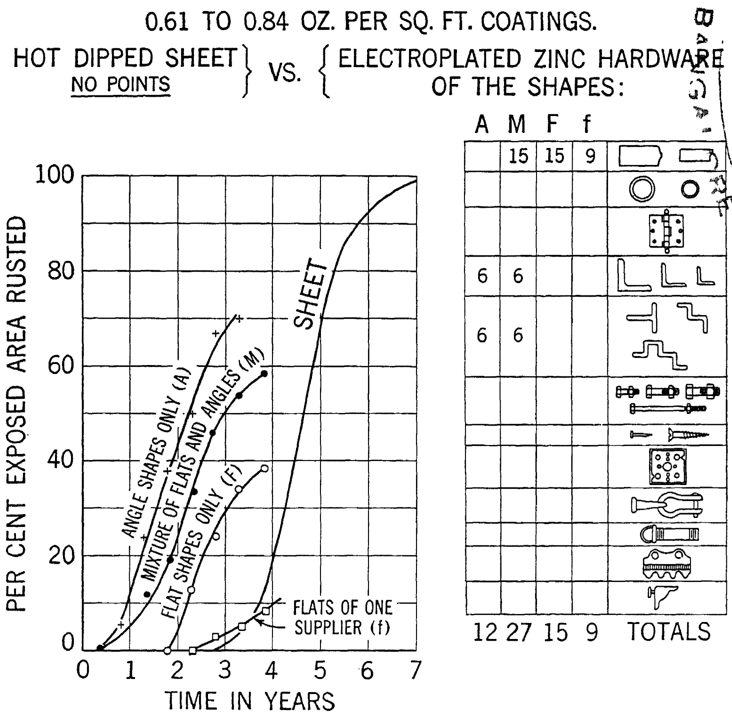


Figure 21.—Comparative Life of Zinc Finishes 1.06 to 0.84 oz. per sq. ft. Effect of Specimen Shape on Life of Plated Zinc.[21]

Apart from the lack of uniformity of the hardware parts it is possible that the surface curvatures of some of these parts is a factor affecting rate of corrosion. It has been shown,[25] for example, in studies of the corrosion of zinc-coated wire for a period of 6 months, that where the wire diameters in inches were 0.015, 0.06, 0.12 and 0.5 the weight losses were in the order 46, 24, 19 and 10 milligrams per sq. in. respectively. Similarly, whereas the rate of corrosion of hot-dipped and sherardized coatings on steel tubes in the New York City atmosphere is approximately 3.5 milligrams per square centimeter per year, based on an exposure period of 2.5

---

[25] Mears, R. B., *Bell Lab. Record,* **11,** 141 (1933).

years, the rate of similar coatings on flat panels is about 2.5 milligrams per square centimeter for the same period.[26]

The electroplated parts exposed in the A. S. T. M. tests were plated, it is understood, in acid sulfate solutions. It is well known that in general zinc coatings produced in this type of bath are somewhat less uniform in thickness than those obtained in alkaline cyanide baths. Moreover the actual rate of corrosion of sulfate zinc coatings in New York City air is reported to be about 1.5 times greater than that of coatings made in the alkaline cyanide solution.[27] This difference is shown in Figure 22 which contains the results of this test (curves 6 and 7) for a longer period of time, as well as other data to be discussed later. In a more recent and somewhat more comprehensive test, which has not been completed as yet, no consistent difference in the behavior of deposits from cyanide and acid-sulfate baths has been found.[24]

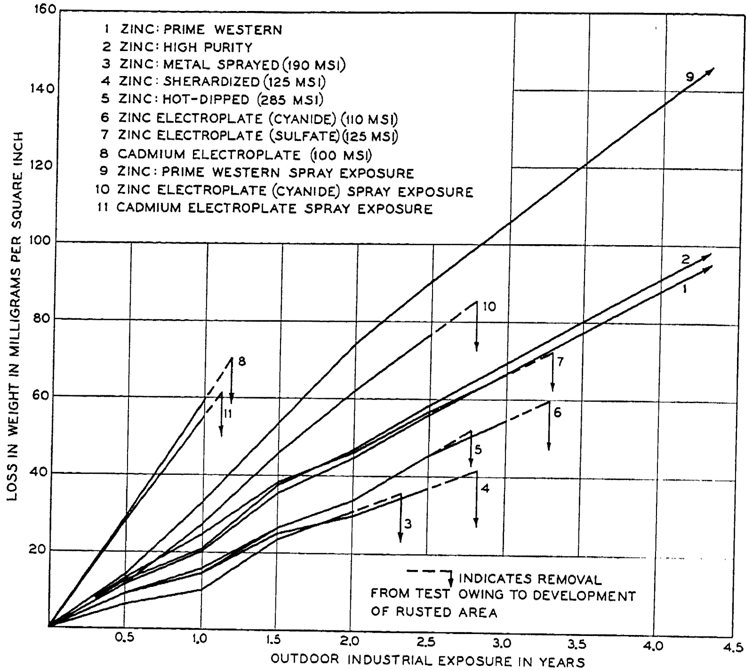


Fig. 22.—Rates of Corrosion of Zinc and Zinc and Cadmium Coatings (Average of 3 Samples).[27]

---

[26] Hippensteel, C. L., Borgmann, C. W., and Farnsworth, F. F., *Proc. Am. Soc. Testing Materials*, 30, Pt. 2, 456 (1930).

[27] Hippensteel, C. L., and Borgmann, C. W., *Trans. Am. Electrochem. Soc.*, 58, 23 (1930).

Effect of Impurities upon Corrosion of Zinc Coatings in the Atmosphere

Atmospheric corrosion tests over a period of five years [28] indicate that antimony and copper are the only two common impurities in zinc which markedly affect corrosion. Antimony in proportions from 0.03 to 0.07 per cent accelerated attack whereas copper in proportions less than 0.06 per cent exerted a protective action. Variations in the cadmium, lead, or iron content had no appreciable effect upon corrodibility of the sheet zinc used, the average composition of which was: lead 1.12 per cent, cadmium 0.10 per cent and iron 0.03 per cent. The presence of small percentages of tin (0.005 per cent) or arsenic (0.09 per cent) did not influence the rate of atmospheric corrosion. Zinc coatings containing lead from 0.5 to 0.8 per cent and iron up to 5.3 per cent were similar in performance to coatings substantially free from these impurities after 30 years' service in a tropical country.[29] In the atmosphere of New York City, Prime Western (97.5 per cent zinc) and High Grade zinc (99.9 per cent zinc) corroded at approximately the same rate in a test carried on over a period of about four years. Figure 22 indicates that the purer grade is slightly more corrodible and this has been confirmed recently in tests of the American Society for Testing Materials.[30] Some evidence has been obtained [31] to the effect that the presence of lead in zinc actually retards the rate of corrosion in the atmosphere, although after a more prolonged exposure it appears that the influence of all the common impurities is negligible.

The results of the galvanic couple corrosion test sponsored by Committee B-3 of the American Society for Testing Materials throw light upon what may be expected to be the effect of metallic impurities in zinc when these impurities are present as separate phases. It will be realized, of course, that the relative areas of impurity and matrix metal may have, owing to polarization effects, some influence affecting the strict application of the couple results to the case under consideration.

The couple test was carried out by clamping together disks of seven common metals in all possible combinations of two metals and exposing these couples to atmospheric corrosion in nine locations. The metals employed were aluminum, zinc, iron, lead, tin, nickel and copper and the test sites were at LaJolla, California, Key West, Florida, and Sandy Hook, N. J., (marine); Pittsburgh and Altoona, Pa., (industrial); Rochester, N. Y., (urban); and State College, Pa., and Phoenix, Arizona, (rural). The results of this test for zinc coupled with the other metals and exposed at the above stations for a period of three years are shown in Figure 23.[32] The solid line through the group represents the average percentage weight loss of two disks of the same metal coupled together as a blank. The

[28] Prost, E., *Rev. Univ. Mines Met.*, 6, 353 (1920).

[29] Argüelles, A. S., *Philippine J. Sci.*, 11, 177 (1916).

[30] Finkeldey, W. H., *Proc. Am. Soc. Testing Materials*, 38, Pt. 1, 195 (1938).

[31] Patterson, W. S., *J. Soc. Chem. Ind.*, 46, 390T (1927).

[32] Hippensteel, C. L., *Proc. Am. Soc. Testing Materials*, 35, Part 1, 167 (1935).

heavy dotted lines indicate the loss of weight of individual disks in the blanks. This percentage loss in weight of the blank is a measure of the normal corrosion rate of this form of specimen of the metal in the respective test exposures. The double cross-hatching illustrates the amount of corrosion of the zinc specimens induced by coupling with the metals shown.

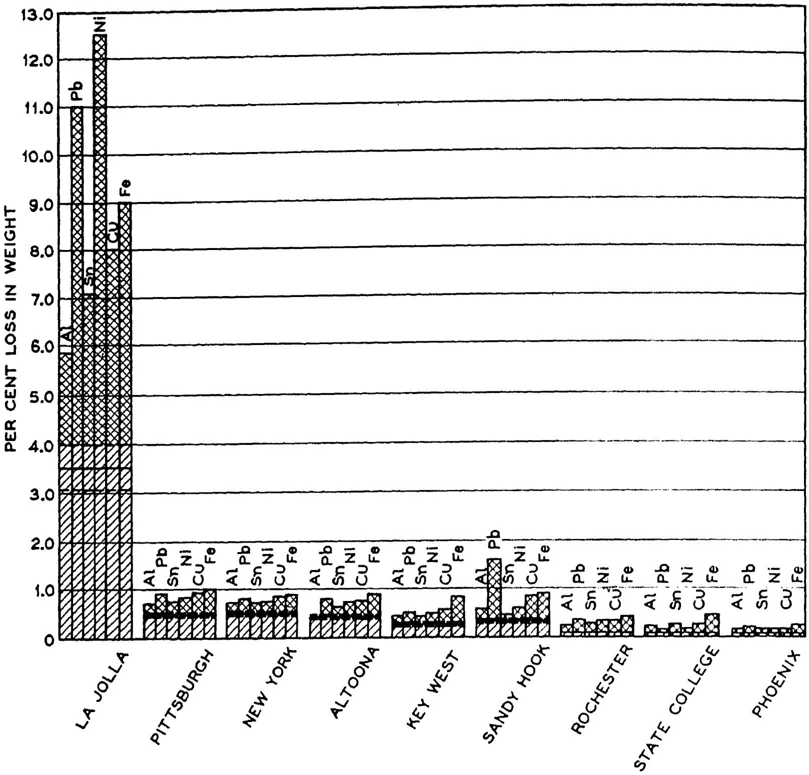


Figure 23.—Galvanic Couple Corrosion in Terms of Percentage Loss in Weight of Zinc after Three Years of Outdoor Exposure.[32]

The most striking result to be observed is the rapid rate of attack at LaJolla and the negligible amount of corrosion at Rochester, State College, and Phoenix. It will be seen further that all the other metals in almost all cases stimulated some galvanic corrosion of zinc. The least effect was obtained when aluminum or tin was the metal coupled with the zinc specimen. Aside from the information which this test provides concerning the effect of contact of other common metals with zinc, there is the definite indication that their presence as impurities in percentages beyond their solid solubility limits may be expected to accelerate corrosion of zinc at least in highly corrosive environments.

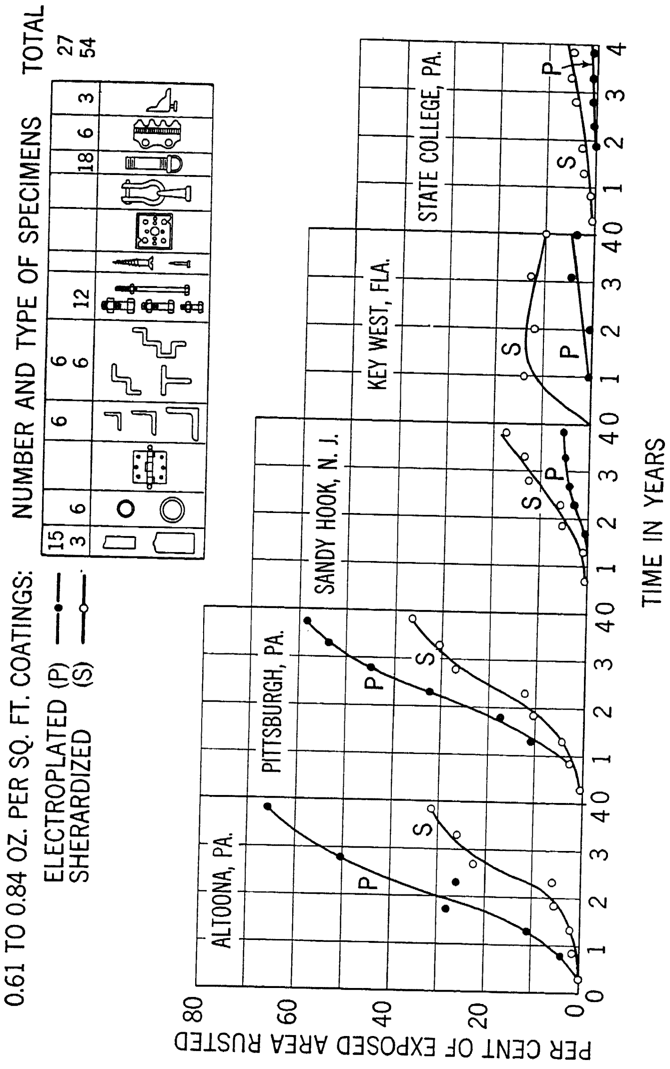


Figure 24.—Life of Zinc Finishes on Hardware, 0.61 to 0.84 oz. per sq. ft. Coatings. (Corresponding to 1.25 to 1.50 oz. per sq. ft. Sheet Coatings.)

regions, calcareous, and that in cities it will be acidic. It is perhaps of interest, therefore, to examine analyses of rain water from pollution gauges situated at four stations where corrosion tests on zinc were made and to record at the same time the values for corrosion. The table on page 105 contains data obtained from 1931 to 1936 at Woolwich, and for shorter periods at Llanwrtyd Wells, Calshot, and Sheffield.[37]

It will be seen from an inspection of these results that there is no correlation between rate of corrosion and amount of rainfall; nor is there any direct correlation between rate of corrosion and the total solids content of the air, although where there is a marked increase in solids content there is a correspondingly large increase in corrosion rate. The pH values obtained for the rain water samples at these four stations do appear, however, to be of significance. It was pointed out in the third paragraph of this chapter that zinc exposed to the atmosphere of highly industrialized regions may not develop corrosion products of basic character, which products, because of their low solubility ordinarily retard corrosion of the metal. In other words, it may well be that rain water of pH 4.3 at Sheffield is sufficiently acidic to prevent the existence of the protective basic film, whereas at Woolwich, where rain has a pH value of 4.8 (and a value of 5 is reported for isolated samples taken independently), this film may develop. At the rural and marine stations the markedly higher values for pH of the rain water ensure corrosion products of basic type.

Conclusions Respecting the Life of Zinc Coatings in Outdoor Atmosphere

The foregoing discussion has considered the factors inherent in the coating and prevalent in the surrounding environment which determine the corrosion behavior of zinc coatings in the atmosphere. In general, it may be concluded that in a given location the life of a zinc coating depends upon its thickness regardless of the method by which the coating is applied. This does not overlook the fact, which has been dwelt upon, that coatings fabricated by the various processes vary in uniformity and may not therefore afford equal protection when coatings of the same average weight are employed. That the life of coatings of comparable uniformity is directly proportional to thickness is well illustrated in Figure 25,[38] in which the per cent of exposed area rusted is plotted against time of exposure for zinc-coated iron and steel sheets exposed at Altoona and Pittsburgh, Pa., and Sandy Hook, N. J.

With respect to the influence of the external or environmental factors on life of zinc coatings it is quite clear that the constituents of the atmosphere in industrial localities, together with humidity and rainfall, are of the greatest importance. The chloride content of sea air apparently has a mild accelerating effect on the corrosion of zinc coatings, particularly in

---

[37] Hudson, J. C., "Fourth Report of Joint Corrosion Committee of the Iron and Steel Institute, the British Iron and Steel Federation, and the Iron and Steel Industrial Research Council," p. 43, London, (1936).

[38] Passano, R. F., *Am. Soc. Testing Materials,* 35, Pt. 1, 167 (1935).

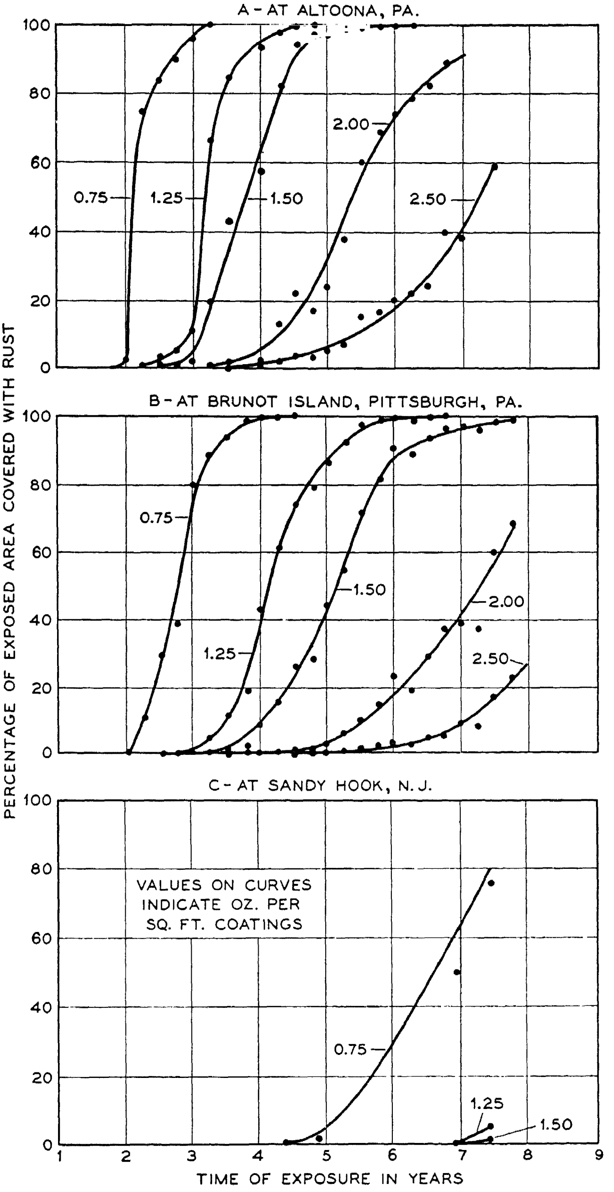


Figure 25.—Progressive Development of Rust on Zinc-Coated Sheets Exposed at Altoona and Pittsburgh, Pa., and at Sandy Hook, N. J.[38]

temperate climates. It is a curious fact, and unexpected, that the life of zinc coatings is appreciably longer in tropical marine locations than in temperate locations of the same type. The best performance of zinc coatings is found in the air of the open inland country. Where the climate is dry, even light coatings furnish protection to ferrous materials for long periods of time. In humid rural sections galvanized products of 1.0 oz. of zinc per square foot of surface (0.0018 inch in thickness) will last a generation.

Any estimation of the life of a protective coating requires a definition as to what is meant by the term life. Where appearance is not an important factor, the useful life of a protective coating is measured in broad terms by the period of time during which the coating prevents failure of the underlying metal. Failure is determined, of course, by the nature of the intended function of the coated article; if it is roofing it may be said to have failed when it becomes perforated and leaks; if it is fence wire it has failed when it breaks, etc. The thickness and corrosion resistance of the base metal are factors, therefore, in the useful life of zinc-coated articles. It has even been suggested [39] that, owing to the rapid corrosion of zinc-coated sheets experienced when moisture accumulates between the sheets in a pile, the life of a corrugated roof may depend largely upon the life of the base metal at the laps.

The definition of the life of zinc-coated iron or steel articles is usually expressed arbitrarily in terms of per cent of the surface showing rust. It may, however, happen that for some purposes a small amount of rust is relatively more significant than a large amount. A method of rating the quality of coatings on a percentage basis in which quality is not taken as proportional to the percentage of unrusted surface, but as a rough logarithmic function of it, has been employed in the atmospheric exposure tests on zinc and cadmium coatings carried on jointly by the American Electroplaters' Society, the American Society for Testing Materials and the National Bureau of Standards.[24] In this system, rusting up to 5 per cent of the surface is given a quality rating of 80 per cent, while surfaces which are on the average 75 per cent rusted are rated as zero in quality. The quality ratings (T) and per cent of surface rusted (R) after an exposure of about 180 weeks in five locations obtained in this test of zinc coatings are given in Table 7. It should be explained that the quality rating (T) is the average rating for the entire period and therefore does not agree directly with (R) the per cent of rust at the end of the period.

It will be observed from an inspection of these more discriminating evaluations of quality that the results are consistent with what would be expected from a knowledge of coating thickness and character of environment.

---

[39] Passano, R. F., Symp. Outdoor Weathering of Metals and Metallic Coatings, *Am. Soc. Testing Materials,* p. 28 (1934).

Table 7.—Quality Ratings and Per Cent of Surface Rusted for Zinc Coatings. 180 Weeks' Exposure to Atmosphere.[24]

Description of Plating Bath	Thickness (mils) (in. × 10^3)	New York		Pittsburgh		Sandy Hook		Key West		State College		Washington	
		T %	R %	T %	R %	T %	R %	T %	R %	T %	R %	T %	R %
Electroplate	0.2	28	75	29	75	53	75	94	3	100	0	96	3
Standard	0.5	53	75	55	75	98	0	93	3	100	0	100	0
Cyanide Bath	1.0	74	55	91	28	98	0	92	3	100	0	100	0
Electroplate	0.2	30	75	22	75	55	75	90	3	100	0	89	60
Cyanide Bath	0.5	60	75	63	75	99	0	93	3	100	0	100	1
with Mercury	1.0	93	3	88	56	99	0	88	3	100	0	100	1
Electroplate	0.2	27	75	23	75	50	75	85	3	100	0	78	75
Sulfate	0.5	49	75	52	75	98	0	86	3	100	0	98	1
Bath	1.0	83	75	91	3	98	0	89	3	100	0	100	1
Electroplate	0.2	28	75	24	75	59	75	89	3	100	0	81	75
Sulfate Bath	0.5	52	75	55	75	97	1	87	3	100	0	100	1
with Dextrin	1.0	83	48	93	4	99	0	86	3	100	0	99	1
Hot Dip	0.9	76	75	86	75	98	3	85	3	100	1	100	1

A rather general estimate of the protective value of zinc coatings on ferrous metals exposed to the atmosphere may be derived from a summary of the experimental results cited in the foregoing discussion and others given elsewhere in the literature.[40] Table 8 contains what appear to be reasonable values for the expected life of zinc-coated products based upon information from these sources. It will be realized that these values are approximate in character and that in actual service exposure conditions may deviate from those considered typical of the atmospheres recorded in this table.

Table 8.—Estimated Life of Zinc-Coated Products in the Atmosphere.

		Life in Years under Atmospheric Conditions					
Thickness in.×1000	Weight in oz./ft.^{2} of Surface*	Rural	Tropical Marine	Temperate Marine	Suburban	Urban	Highly Industrial
3.6	2.00	50	40	35	30	25	15
2.3	1.25	35	30	25	20	17	9
1.8	1.00	25	20	15	12	10	7
1.1	0.60	10	8	7	5	4	3
0.66	0.37	7	6	5	4	3	2
0.44	0.25	5	4	3	3	2	1

* In the case of galvanized steel sheets the weight of zinc is specified in terms of total zinc on both sides of the sheet; *i.e.*, a 2-oz. sheet has 1 oz. of zinc per sq. ft. of surface. Consequently in estimating the life of galvanized sheet in the light of data given in this table, the specified weight and thickness values for the sheet should be halved.

Performance of Zinc Coatings in Indoor Atmospheres

Zinc coatings are used indoors for the protection of iron and steel articles where appearance is not a primary factor. It is well known that zinc coatings darken to an unpleasing gray color and that electrodeposited coatings in particular "fingerprint" and stain. The new "bright" zinc coatings provide a marked improvement from the standpoint of appearance although darkening to some extent and "spotting" may appear in some cases in these coatings.

The atmosphere indoors corresponds in a general way to that prevailing outside in a given locality. Variations in humidity and temperature, are, of course, somewhat less extreme and there is no rainfall indoors to dissolve and remove soluble corrosion products.

The manner in which zinc corrodes in the atmosphere when protected from rain was mentioned on the first page of this chapter. It was stated that in atmospheres of moderate humidities, such as prevail rather generally indoors, the corrosion of zinc, measured as gain in weight with time, follows a linear relationship after the first few hours. The slope of the weight-gain-time curve increases somewhat with humidity and with atmospheric pollution. At relative humidities above about 75 per cent this curve becomes slightly concave upward, indicating electrolytic action. Zinc of exceptionally high purity prepared by fractional distillation *in vacuo* and containing less than one part of impurity in ten thousand does not corrode or tarnish in laboratory air.[41]

---

[40] Hubbell, J. P., and Finkeldey, W. H., *Trans. Am. Inst. Chem. Eng.*, 18, 51 (1926); also, Anderson, E. A., *Mech. Eng.*, 58, 799 (1936).

The corrosion of zinc coatings indoors is of the same general character as it is in outdoor exposures protected from rain. The presence of pores in the coating may result in the appearance of electrolytic action at somewhat lower relative humidities but usually there is little evidence of this type of attack. Indeed at low humidities indoors superficial rusting of iron is sometimes observed at pinholes in coatings, the thickness of which is of the order of 0.0002 inch. Porous zinc coatings do, however, in most instances provide adequate protection to ferrous articles exposed indoors and in so doing must undergo slow, although not very visible, sacrificial action. In general, it may be assumed that the protective life of zinc coatings indoors is at least fivefold greater than that of coatings of the same thickness exposed to the outdoor atmosphere in the same locality.

The darkening of zinc coatings with time does not affect their protectiveness. A coating of clear lacquer is sometimes applied to improve appearance of zinc-coated articles. This treatment produces a somewhat darker cast but arrests further change in this direction and prevents "fingerprinting."

The use of mercury proposed a few years ago [42] to improve the appearance of zinc-plated coatings resulted in some instances in the development of black spots on the surface. In other cases when appreciable amounts of mercury were deposited in the coating, actual droplets of mercury "sweated" out in time on the surface of coating and became very conspicuous against the darkening zinc areas. It is claimed that these difficulties with mercury have been overcome by using minimum and controlled quantities of this metal in the plating operation.

Performance of Zinc Coatings in Submerged Exposures

More work has been reported on the corrosion of zinc than on coatings of zinc under conditions of submersion or partial submersion in water and liquids. Most of this experience with zinc is, however, directly applicable to zinc coatings during at least that portion of the life of the coating when it is reasonably continuous. In submerged corrosion, electrolysis plays a larger part in the performance of the coating than it does in atmospheric exposure, and similarly corrosion products are even more important in determining the rate and character of corrosion under these conditions. Much of the material concerning the effect of type of coating and composition of coating on corrosion which is given in the preceding pages applies equally well to the behavior of zinc coatings in aqueous media.

Behavior of Zinc Coatings in Natural Waters

Zinc is not corroded to a measurable extent in pure water free from oxygen and carbon dioxide.[43] That some action does occur is evident

[41] Cyr, H. M., *Trans. Electrochem. Soc.*, 52, 349 (1927).

[42] Wernlund, Ç. J., *Trans. Amer. Electrochem. Soc.*, 45, 273 (1924).

[43] Bengough, G. D., Stuart, J. M., and Lee, A. R., *Proc. Roy. Soc., London*, A 121, 88 (1928).

from the fact that when zinc dust (which provides a large metallic surface area) is placed in water at ordinary temperatures for several hours, hydrogen is evolved.[44] When air or oxygen is present in water corrosion is accelerated owing to the depolarization of cathodic areas which ensues. After an interval of time, depending upon circumstances, the process becomes retarded by the formation of zinc hydroxide which occurs as a result of the reaction of zinc ions with hydroxide ions produced at cathodic areas. This product, hydrated to various degrees, is precipitated in gelatinous form, but may in time become crystalline in character. The rate of corrosion of zinc in pure water containing oxygen is generally controlled by the rate of diffusion of oxygen through this film of corrosion products. Zinc hydroxide is of a low order of solubility. If the water contains carbon dioxide, a slightly more soluble product, basic zinc carbonate, is formed. At higher pressures of carbon dioxide, the normal carbonate, still more soluble, becomes the normal solid phase. The effect of the presence of carbon dioxide in waters, then, is to increase their corrosiveness toward zinc and zinc-coated iron and steel. The corrosion products which can be assumed to be basic carbonates in most instances are less protective than zinc hydroxide.

The protectiveness of the film formed on zinc-coated cisterns and water pipes exposed to domestic waters depends upon many variables. Very likely the degree of hydration, crystalline structure, colloidal dispersion and the presence of other salts are all factors affecting the nature of the film. In general, although substances such as nitrates, and sulfates and chlorides in small concentrations increase the corrosiveness of water, it is well known that most domestic waters are less corrosive to zinc than is distilled water. Among the protective constituents present in natural waters are anions, such as carbonates and silicates, which form zinc salts of relatively low solubility and are precipitated in close contact with the metallic surface. Higher concentrations of sulfates appear to improve protection.

The more rapid corrosion of galvanized pipes and water tanks by hot water is attributable to the effect of temperature on the character of the corrosion products.[45] Up to 50° C. the rate of corrosion of zinc in aerated distilled water increases slowly with increasing temperature. At 53° C. the rate of attack increases abruptly, reaching a maximum at 65° C. above which it decreases rapidly. In the range from 20 to 50° C. the corrosion products are gelatinous and adherent, but above 55° C. they become granular and non-adherent. Beyond 65° C. the film of corrosion products becomes more dense and at 100° C., where rate of corrosion is small, the film is compact, glossy and very adherent.

The hydrogen-ion concentration of water and aqueous solutions has a marked effect upon their corrosiveness toward zinc and zinc coatings. This is well illustrated in Figure 26[46] in which the average overall penetration in centimeters per year is plotted against hydrogen-ion concentration expressed in terms of pH. It will be seen that the pH range 6 to 12.5 is characterized by the development of a stable film of corrosion products, the presence of which insures a low rate of corrosion, and furthermore, that on either side of this range the film is unstable and the corrosion rate high. The pH range of most natural waters used for domestic purposes is approximately 5.8 to 8.5, and were such waters free from carbon dioxide, there would be little corrosion of zinc-coated pipes by them at normal temperatures. In general, the effect of the presence of carbon dioxide in waters will be to displace upward the curve given in Figure 26. Experience has shown that waters, the values of pH of which are below 6.5, corrode galvanized iron readily. This may be associated with the observation that the products of corrosion lose their crystalline character below pH 6.4.[47]

---

[44] Van Rijn, W., *Chem. Weekblad,* 5, 1 (1908).

[45] Cox, G. L., *Ind. Eng. Chem.,* 23, 902 (1931); *see also* Maconachie, J. E., *Trans. Electrochem. Soc.,* 66, 213 (1934).

[46] Roetheli, B. E., Cox, G. L., and Littreal, W. B., *Metals and Alloys,* 3, 73 (1932).

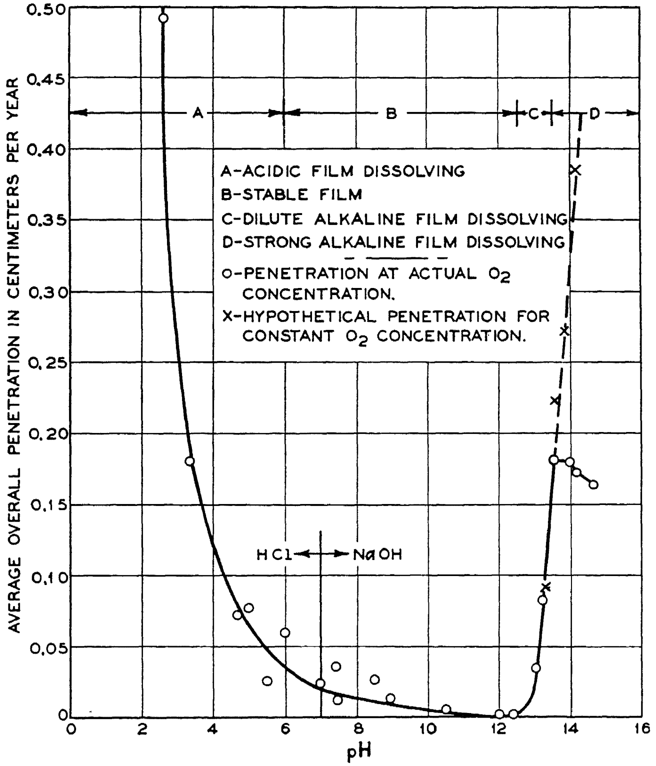


Figure 26.—Corrosion of Zinc as a Function of pH.[46]

---

[47] Baylis, J. R., *Amer. Water Works Assoc.*, **15**, 598 (1926).

It should not be assumed that the nature of the film of corrosion products which forms on zinc is the only factor affecting corrodibility over the range of hydrogen-ion concentration under discussion. The oxygen concentration, for example, will vary. The depression shown in the actual rate of corrosion in the high alkaline range is the result of decreasing oxygen solubility. Another factor influencing rate of corrosion is undoubtedly the magnitude of the potentials of the corrosion cells at the metallic surface. The well known fact that zinc displaces hydrogen from both acids and alkalies suggests that the potential difference of the zinc-hydrogen cell is of somewhat similar magnitude over the range of hydrogen-ion concentrations from acid to high alkali. Actual measurements have shown that the potential difference of this cell from approximately pH 5 to pH 12 is about 0.3 volt.[48] In other words, the reduction of hydrogen-ion concentration over this range is accompanied, owing to the formation of zincate, $(ZnO_2)^{--}$ ions, by a corresponding reduction in zinc ion concentration.

The character of the corrosive attack of natural waters upon galvanized iron depends mainly upon the composition of the water. There is usually less pitting in galvanized iron pipes than in bare iron and steel pipes. In waters of pH 7.5 to 9.5 containing calcium bicarbonate but low concentrations of sulfates, chlorides and nitrates, the attack on zinc is negligible, owing to the formation of a carbonate film of high continuity and low solubility on the metallic surface. In waters low in temporary hardness (*i.e.,* calcium bicarbonate) or containing appreciable concentrations of sulfates, chlorides or nitrates, zinc-coated iron is likely to suffer a pitting form of attack.[49]

The thickness of zinc coatings in water pipes and storage tanks required to prevent "red water," or rusting of the underlying iron, depends upon the hardness of the water. In general, much thicker coatings are needed in soft water than in hard water.[50] There is evidence that in water of a given character there is a critical minimum thickness below which the protective life of the coating will be very short.[49] For example, in waters containing calcium bicarbonate the anodic dissolution of zinc is accompanied by the development of a film of basic zinc carbonate at anodic areas and a film of calcium carbonate on exposed iron areas. The formation of these films reduces the rate of solution of zinc. In other words, in any given water the thickness of the zinc coating should be sufficient to provide for the construction of a protective layer of corrosion products before all the zinc is dissolved. For the average city water supply, coating thicknesses of zinc of 0.0017 inch[51] and 0.002 inch[52] have been recommended as necessary for protection of iron and steel pipe.

---

[48] Measurements by Dr. R. B. Gibney of Bell Telephone Laboratories.

[49] Britton, S. C., *J. Soc. Chem. Ind.,* 55, 19T (1936).

[50] See Evans, U. R., "Metallic Corrosion, Passivity and Protection," p. 574, London, Edward Arnold & Company, 1937.

[51] Friedli, *J. Chem. Zentr.,* 103, 3108 (1932).

[52] Naumann, *Gas u. Wasserfach.,* 77, 403 (1934).

Corrosion of Zinc Coatings in Sea Water and Chloride Solutions

Steel armor wires used to support and protect submarine cables are zinc-coated. While it is true that additional protection in the form of asphalt and jute coatings, as well as of sea-bottom ooze, is provided in this exposure, the use of zinc seems to be a factor in the long life of these structures. From an inspection of galvanized wire-armored harbor cables after a period of submersion it is evident that the jute covering by enclosing the armor wire restrains free circulation of water and permits the stagnant solution near the surface of the wire to become saturated with zinc corrosion products. In other words, the presence of the jute covering is conducive to the formation of a protective film on the galvanized wire.

The exposure of bare zinc surfaces to sea water under conditions in which there was no restriction on the availability of oxygen gave greater evidence of attack. After a four-year exposure to sea water in the Bristol Channel a galvanized iron bar lost less weight than either iron or zinc bars employed in the same test.[53] The zinc specimen, while covered for the most part with a tenacious layer of corrosion products, displayed numerous dome-shaped excrescences beneath which the metal was pitted. Electroplated zinc coatings of the order of 0.0005 inch in thickness have been shown to afford considerable protection to aluminum and Duralumin over a period of 12 months when subjected to sea-water spray and intermittent immersion in sea water.[54] Laboratory studies on zinc foil immersed in sodium chloride solutions have shown that the maximum attack occurs in a solution containing 0.5 per cent sodium chloride and that in a 3-per cent solution of the salt, corresponding approximately to sea water, the rate of corrosion was lower and of the same order as in fresh water.[55] Incidentally the results which are obtained in corrosion tests of this type depend to a large extent upon the conditions under which the test is carried out.

Careful studies made of the corrosion of zinc in water and potassium chloride solutions,[56] under conditions of complete submersion in a vessel of given dimensions, show that in pure water and in solutions of chloride concentrations less than twenty thousandths normal, reaction occurs without the evolution of measurable quantities of hydrogen. At concentrations of potassium chloride greater than ten thousandths normal, hydrogen was always evolved except when highly purified zinc[57] was used; in the range ten thousandth to tenth normal potassium chloride, from 5 to 15 per cent of the total corrosion was accompanied by hydrogen evolution. Up to concentrations of fiftieth normal the rate of corrosion increases in proportion to the salt concentration, there being an excess of oxygen present. Beyond tenth normal concentration, the rate of corrosion decreases owing to the decreasing solubility of oxygen in the more concentrated solutions. In these studies the shape of the curve obtained by plotting rate of corrosion against salt concentrations depended to a large extent upon the conditions of the experiment.

---

[53] Friend, J. N., *J. Inst. Metals*, **39,** 111 (1928).

[54] Sutton, H., and Sidery, A. J., *J. Inst. Metals*, **38,** 241 (1927).

[55] Friend, J. N., and Tidmus, J. S., *J. Inst. Met.*, **31,** 177 (1924).

[56] Bengough, G. D., Stuart, J. M., and Lee, A. R., *Proc. Roy. Soc., London,* **A 116,** 425 (1927); **A 121,** 88 (1928); **A 127,** 42 (1930); **A 131,** 494 (1931).

[57] Specimen furnished by the New Jersey Zinc Company prepared by fractional distillation and containing less than 0.0001 per cent of impurities.

The availability of oxygen is an important factor affecting both the rate and character of corrosion of zinc and zinc coatings in salt solutions. Laboratory tests made upon specimens of zinc partially immersed in potassium chloride solutions, instead of completely submerged as in the experiment described above, showed, in contrast to that experiment, that the rate of corrosion continued to rise with increasing salt concentration throughout the range of concentrations employed in the two investigations.[58]

The "water-line" in galvanized tanks and cisterns is a region often particularly susceptible to corrosive attack. With waters high in chlorides and containing sulfates, carbonates and nitrates, pitting action has been observed at the water-line, and also at the bottom of the tank.[59] Laboratory studies in which zinc was partially immersed in chloride solutions have shown that the metal is first immune at the water-line but corroded lower down, but that after a more extended period of exposure intense attack occurred at the water line.[60]

The explanation of this behavior,[61] which appears to account for water-line attack in galvanized cisterns as well, lies in the operation of a differential aeration cell. The area just beneath the surface of the solution, being more accessible to oxygen, becomes cathodic to the area lower down which, being anodic, begins to corrode. In the operation of this cell in the presence of alkali chlorides there is an accumulation of alkali in the aerated zone which, until it attains high concentration (corresponding to a high value for pH), results in the development of a protective film. It has been observed that water-line pitting becomes more pronounced in $2N$ and N potassium chloride than in 0.1 or $0.01N$ solutions.[58] Obviously, higher chloride concentrations permit the production of higher concentrations of alkali with greater probability of destruction of the protective film and pitting action.

In the water-line pitting of chloride-bearing waters it is possible that other constituents which are film-forming, such as carbonates and sulfates, if present in only moderate concentrations, contribute to pitting by providing a film of corrosion products which is discontinuous in character.

Effect of Impurities upon Corrosion of Zinc in Acids

The presence in zinc or zinc coatings of any metallic impurity which discharges hydrogen more readily than does zinc itself would be expected to increase corrodibility. It has been observed that antimony, copper and iron, which fall in this class, do accelerate the corrosion of zinc in dilute sulfuric acid.[62] Lead and cadmium, unless present in more than the usual amount, have a negligible effect.[63] Indeed these elements have been shown to reduce the accelerating effect of antimony.[64] Small amounts of aluminum do not affect the corrosion of zinc in acid solutions.[65]

---

[58] Borgmann, C. W., and Evans, U. R., *Trans. Electrochem. Soc.*, 65, 257 (1934).

[59] Richards, H. F., *Iron and Steel Inst.*, 1, 183 (1928).

[60] Bengough, G. D., and Wormwell, F., *Proc. Roy. Soc., London*, A 140, 402 (1933).

[61] For an excellent discussion of the mechanism of water-line corrosion see *Evans, J. Soc. Chem. Ind.*, 55, 210 (1936).

High purity zinc containing less than 0.0001 per cent of impurities is very resistant to attack by hydrochloric and sulfuric acids but corrodes readily in nitric acid.[66] Apparently nitric acid provides cathodic areas, probably a species of oxygen electrode on the pure zinc surface, which enables the metal to realize its natural tendency to corrode.

Performance of Zinc Coatings in Soils

Zinc coatings are commonly employed for the protection of steel anchor rods, culverts and similar structures against corrosion. In these cases a considerable proportion of the metallic surface is exposed to soils. Experience has shown that zinc coatings furnish considerable protection to ferrous metals in many soils, the exceptions being highly alkaline soils of a high chloride content and highly acid soils. In the former soils serious corrosion of galvanized anchor rods often occurs near the ground-line, a behavior suggestive of the water-line attack which sometimes occurs inside galvanized cisterns and has just been described.

Probably no environment in which metals are used is more complex and more varied than that provided by soils. Soils consist of a great variety of complex silicates and mineral residues ranging in particle size from colloidal clay to sand and gravel. They contain free and adsorbed salts, acids or bases and an admixture of organic matter. Soil structures are more or less permeable to moisture and air. At intervals following rains, water dissolves soluble constituents and seeps away at a rate which depends upon the texture of the soil and the slope of the terrain. Soils possess atmospheres which contain somewhat less oxygen but more carbon dioxide than the air above ground. There may be present also hydrogen sulfide, organic acid vapors, methane and various decomposition products of organic matter. Soil microörganisms and fungi are always present and these may influence acidity or the reducing or oxidizing nature of the environment.

Metals buried in soils are subject, then, to a most heterogeneous set of conditions which may vary from time to time depending upon the weather and other circumstances. Physical contact with soil particles is sometimes a factor in the production of corrosion cells of the differential aeration type.[67]

The most extensive and systematic test of the corrodibility of metals in soils is that sponsored by the National Bureau of Standards in 1922 and carried on over a period of more than twelve years. Originally this test was primarily designed to investigate the corrodibility of ferrous pipes in soil in the absence of stray electrical currents. It was later expanded to test approximately 9000 non-ferrous specimens including zinc and zinc-coated iron and steel. Something like ninety different soils were employed in this program of tests, although not all the metallic materials were buried in all of the soils.[68]

---

[62] Vondrácek, R., and Izák-Krizko, J., *Rec. trav. chim.*, 44, 376 (1925).

[63] Prost, E., *Bull. Soc. chim. Belg.*, 28, 94 (1914).

[64] Patterson, W. S., *J. Soc. Chem. Ind.*, 45, 325T (1926).

[65] Harris, F. W., *Trans. Electrochem. Soc.*, 57, 313 (1930).

[66] Cyr, H. M., *Trans. Amer. Electrochem. Soc.*, 52, 349 (1926).

[67] Burns, R. M., and Salley, D. J., *Ind. Eng. Chem.*, 22, 293 (1930).

The rates of loss of weight and depth of penetration observed after ten years of burial of specimens of sheet and cast zinc in five soils is given in Table 9.[69]

Table 9.—Rates of Loss of Weight and Depth of Penetration of Zinc Buried Approximately 10 Years.[69]

	Soil 13		Soil 29		Soil 42		Soil 43		Soil 45	
	Loss	Pits	Loss	Pits	Loss	Pits	Loss	Pits	Loss	Pits
Sheet Zinc (99.5%)	0.35	4.0	0.46	3.9	0.085	1.7	0.23	3.3	f	f
Cast Zinc (99.5%)	.34	7.0	.53	5.5	.078	1.8	.22	6.8	0.94	9.8
Sheet Zinc (Standard)	.19	5.2	.38	f	.11	2.0	.45	3.7	f	f

Note: Loss of weight is expressed in ounces per square foot per year, and maximum penetration in mils per year. f = failure of one or more holes. Dimensions of sheet stock was 6 × 2 × 0.06 inches and cast stock 6 × 2 × 0.25 inches. Composition of material designated as "standard" is unknown but probably less pure than the other specimens of known composition.

The characteristics of these soils are given in Table 10.[70] It will be observed that the rate of corrosion of zinc in the alkali soils (Soils 13 and 45) and the acid muck (Soil 29) is the most severe, the tidal marsh (Soil 43) being next in order. These soils are also very corrosive toward ferrous materials. The remaining soil, (Soil 42), although markedly acid, is probably more representative of the average soil in regions of high rainfall and the results from this location show up very favorably for zinc. The average loss of weight of ferrous specimens at this location was approximately tenfold greater, and rate of pitting fivefold greater than for zinc during the same period.[71]

A more accurate idea of the protection afforded by zinc coatings against soil attack may be obtained from the results reported for the behavior of galvanized pipe and sheet included in the Bureau of Standards test of specimens buried in 1924. The coated pipes were 17 inches long and from 1½ to 3 inches in diameter, and the sheets were mostly 16-gauge metal 6 inches wide and 12 inches long. Most of the specimens carried 2-ounce coatings of zinc applied by the hot-dip process. The ferrous base materials employed were open-hearth iron pipe and sheet, Bessemer steel sheet and

---

[68] Logan, K. H., Ewing, S., and Yeomans, C. D., *Bureau of Standards Technologic Paper No. 368* (1928).

[69] Logan, K. H., *Bur. Standards J. Research*, **17**, 781 (1936).

[70] Compiled from data given in reference 69.

[71] Logan, K. H., and Taylor, R. H., *Bur. Standards J. Research*, **12**, 119 (1934).

Table 10.—Properties of Soils in National Bureau of Standards Soil Corrosion Test of Zinc and Zinc Coatings.[70]

Soil No.	Soil Type	Location	Mean Temperature (° F.)	Annual Precipitation (inches)	Drainage of Test Site	Moisture Equivalent (%)	pH	Total Acidity Mg-eq. per 100 g. of Soils	Resistivity at 60° F. (ohm-cm.)	Composition of Water Extract mg-eq. per 100g. soil						
										Na+K as Na	Ca	Mg	CO_3	HCO_3	Cl	SO_4
1	Allis silt loam	Ohio	49.2	33.8	P	26.6	7.0	11.4	1215	0.72	0.25	0.43	0.00	0.09	0.09	0.83
3	Cecil clay loam	Ga.	61.2	48.3	G	29.1	5.2	11.5	30000	...	...	...	...	...	...	...
8	Fargo clay loam	N. Dak.	39.0	21.0	P	37.0	7.6	A	350	1.42	1.72	2.55	0.00	0.71	.01	4.43
11	Hagerstown loam	Md.	55.4	42.6	G	32.0	5.3	10.8	11000	...	...	...	...	...	...	...
13	Hanford fine sandy loam	Calif.	64.6	5.6	F	21.7	9.5	A	290	6.23	.09	.13	0.00	1.12	1.64	3.76
14	Hempstead silt loam	Minn.	44.2	27.2	F	17.2	6.2	5.6	3520	...	...	...	...	...	...	...
16	Kalmia fine sandy loam	Ala.	67.3	61.6	F	22.2	4.4	11.8	8290	...	...	...	...	...	...	...
18	Knox silt loam	Neb.	50.6	27.8	G	28.4	7.3	1.4	1410	.27	.63	.20	0.00	.94	0.00	.25
19	Lindley silt loam	Iowa	49.5	32.0	G	28.4	4.6	10.9	1970	.38	.32	.41	0.00	.16	.03	.46
20	Mahoning silt loam	Ohio	49.2	33.8	P	22.4	7.5	1.5	2870	.25	.48	.20	0.00	.51	0.00	.15
22	Memphis silt loam	Tenn.	61.6	47.7	G	28.4	4.9	9.7	5150	...	...	...	...	...	...	...
23	Merced silt loam	Calif.	65.0	6.0	P	24.7	9.4	A	278	8.38	.38	.22	.02	1.87	1.12	5.57
28	Montezuma clay adobe	Calif.	61.0	10.3	P	24.6	6.8	C	408	1.50	.06	.18	.00	.12	.99	.89
29	Muck	La.	69.3	57.4	VP	34.5	4.2	28.1	1270	2.15	1.92	1.55	.00	.00	1.69	2.30
32	Ontario loam	N.Y.	47.6	32.8	G	17.8	7.3	0.5	5700	.23	.70	.12	.00	.73	.01	.42
33	Peat	Wis.	46.1	30.1	VP	72.8	6.8	36.0	800	1.52	7.30	4.06	.00	C	2.27	2.13
37	St. John's fine sand	Fla.	69.3	47.4	P	7.0	3.8	15.3	11200	...	...	...	...	...	...	...
39	Sassafras silt loam	Del.	54.0	40.0	P	24.2	5.6	6.6	7440	...	...	...	...	...	...	...
40	Sharkey clay	La.	69.3	57.4	P	33.0	6.0	9.4	970	.56	.58	.44	.00	.93	.07	.28
42	Susquehanna clay	Miss.	64.0	53.0	P	34.8	4.7	28.2	13700	...	...	...	...	...	...	...
43	Tidal marsh	N. J.	52.0	43.0	VP	55.4	3.1	36.8	60	45.10	5.17	9.45	.00	.00	43.30	37.00
45	Alkali soil	Wyo.	47.2	15.3	P	14.8	7.4	A	263	8.15	3.70	.70	.00	.24	.18	11.98
46	Sandy loam	Colo.	50.0	14.1	G	7.6	7.0	C	1500	...	...	...	...	...	...	...

Notes: A = Alkaline; C = Not determined; G = Good; Mg-eq = milligram equivalent; F = Fair; P = Poor; VP = Very poor.

open-hearth steel containing 0.2 per cent copper. The results obtained at the end of approximately eight years in 23 soils are recorded in Table 11.[71] The properties of these soils are given in Table 10. Later results after burial for about 10 years in 43 soils are in substantial agreement with the results given in Table 11.[71a]

Table 11.—Corrosion of Galvanized Pipe and 16-Gauge Sheet.

Soil No.[1]	Duration of test (years)	Rate of loss of weight in ounces per square foot per year				Rates of penetration in mils per year [6]				Condition [7]			
		A (pipe)[2]	A3 [3]	B [4]	Y3 [5]	A	A3	B	Y3	A	A3	B	Y3
1	8.62	0.332	0.350	0.396	0.403	....	1.28	1.97	2.09	U	P	U	U
3	8.13	.038	.035	.034	.030	....	.74	.62	.62	E	R	R	E
8	8.73	.057	.033	.032	.035	....	....	....	....	E	E	E	E
11	8.66	.048	.029	.051	.047	....	2.42	2.89	3.23	R	P	P	P
13	8.25	.140	.207	.080	.238	....	1.82	.61	1.82	E	P	R	U
14	8.76	.028	.014	.014	.015	....	....	....	....	E	E	E	E
16	8.06	.333	.106	.161	.095	....	1.61	1.74	1.61	E	U	P	P
18	8.60	.029	.016	.015	.021	....	....	....	....	E	E	E	E
19	8.59	.069	.028	.040	.034	....	....	1.05	....	E	E	R	R
20	8.62	.141	.146	.306	.104	....	1.97	2.78	.81	R	P	P	U
22	7.97	0.98	....	....	....	....	....	....	....	R	...	...	...
23	8.25	[9].945	.358	.260	.628	[9]6.67	3.58	2.12	4.00	P	P	P	P
28	7.73	[8].177	.463	.082	.066	....	5.95	.91	.65	E	P	U	R
29	8.10	[8].484	.286	.554	.390	1.98	4.94	3.21	4.70	P	P	P	P
32	8.63	.037	.026	.020	.022	....	....	....	....	E	E	E	E
33	8.63	.171	.171	.213	.182	....	1.85	1.97	1.62	U	P	P	P
37	8.06	.233	.338	.396	....	....	2.61	2.23	....	R	P	P	P
39	8.51	....	.113	.156	.107	....	2.35	1.88	2.00	...	P	P	P
40	8.09	.073	....	....	....	....	....	....	....	E	...	...	...
42	8.08	[8].036	.028	.027	.029	....	....	....	....	E	E	R	E
43	8.63	[8].114	.068	.155	.100	....	.81	3.82	.58	E	U	P	U
45	8.70	[8].284	.057	.302	.078	....	1.03	4.95	.69	U	U	P	U
46	8.69	.048	.008	.005	.007	....	....	....	....	E	E	E	E

Notes: 1. See Table 10 for description of soils.
2. A = pure open-hearth pipe.* Coating = 2.82 oz./ft.^{2}
3. A3 = pure open-hearth iron sheet.** Coating = 1.98 oz./ft.^{2}
4. B = Bessemer steel sheet. Coating = 1.62 oz./ft.^{2}
5. Y3 = open-hearth steel sheet, 0.02 per cent copper. Coating = 2.15 oz./ft.^{2}
6. Maximum penetration obtained by averaging deepest pit on each side of sheet.
7. Symbols: U = Uniformly corroded.
E = Excellent.
R = Rusted.
P = Pitted.
8. Average of 2 specimens.
9. Average of 3 specimens.

* For analysis see *Bur. Standards Tech. Paper* No. 368, p. 515.

** As is customary, the weight of coating given for the pipe samples is the weight of zinc on the outside of the pipe, whereas the weight given for the sheet is the total weight of zinc divided by the area on one side of the sheet. Hence a 2-oz. coating on pipe in this table is twice as thick as a 2-oz. coating on a sheet.

From an examination of the corrosion results it is apparent that there is no significant difference in the corrosion-resisting properties of the specimens which can be attributed to the character of the ferrous base material. There is some indication that the specimens with the lightest weight of coating (those designated as B groups) rusted somewhat more readily than the heavier coatings, a result which was obtained more conclusively in an additional test carried out in six of these soils over a period of six years using specimens of a wider range of coating thicknesses.

In general these studies have shown that zinc coatings provide considerable protection to iron and steel. A comparison of average rates of loss of weight of zinc-coated and bare ferrous specimens in these soils over a period of eight to ten years shows that the latter corrode 5.6 times more rapidly than do the zinc-coated specimens. This is based on the average rate of loss of weight of 0.148 ounce per square foot per year for all zinc-coated specimens in all soils, as against 0.840 ounce per square foot per year for all ferrous samples in the same soils.[71]

[71a] Logan, K. H., and Ewing, S. P., *J. Research, Nat. Bur. Standards*, **18**, 361 (1937); R P 982.

An accurate correlation of rates of corrosion with soil characteristics is difficult owing to the different relative influence of the numerous and complex variables in soil exposures. From an inspection of the data of Table 11 it may be seen that the soils may be classified, with respect to corrosiveness toward zinc coatings, into three groups: mildly corrosive, moderately corrosive, and severely corrosive. In the first group exhibiting least attack are soils 3, 8, 11, 14, 18, 19, 32, 42 and 46. These soils, with the exception of 3, 11 and 42, are in areas of low rainfall and at sites where the drainage is good. All are of moderately high electrical resistivity and low salt content (where data are available) except soil number 8, which is low in resistivity and high in sulfates. The average loss in weight for all zinc-coated specimens in these soils was 0.030 ± 0.009 ounce per square foot per year, and the rate of penetration 1.50 ± 0.86 mils per year.

In the group of soils of intermediate corrosiveness toward zinc-coated specimens are soils 13, 16, 20, 28, 33, 39, 43 and 45. These were for the most part poorly drained and high in salt content. The average annual loss of weight for all specimens in these soils was 0.155 ± 0.03 ounce per square foot, and the average annual penetration 1.84 ± 0.2 mils.

The poorest performance of zinc coatings was in soils 1, 23 and 29. These were all poorly drained and of low resistivity. The first was neutral and of moderate salt content, but the second, soil 23, was highly alkaline and the third highly acid in character. Both 23 and 29 were high in alkali sulfates. The values for average annual loss in weight were 0.45 ± 0.07 ounce per square foot and the average annual penetration 3.16 ± 0.9 mils per year.

In view of the foregoing analysis of soil corrosion results it is possible to make rough estimates of the life of zinc coatings in soils representative of the three classes of corrosiveness. The life in a given soil or soil type appears to be proportional to the thickness of coating in much the same manner as in atmospheric exposure. Assuming that a reasonable criterion of the protective value of zinc coatings in soils is the period during which rusting is prevented over the major area of the ferrous metal surface, and allowing for about 20 per cent variation in thickness of coating, it is possible to make the following estimates of the life of zinc coatings of one ounce per square foot of surface area in soils of the three degrees of corrosiveness described above.

Corrosiveness of Soil	Life of Coating of 1 oz./ft.^{2}
High	1-2 years
Moderate	4-6 years
Mild	18-25 years

Protective Value of Zinc Coatings Against Corrosion Fatigue of Steels

Steels and many other metals when subjected under certain circumstances to repeated stresses may develop fatigue cracking. It became recognized a few years ago [72] that the nature of the environment affects the endurance of metals to such stressing, and the term, "corrosion-fatigue" was applied to the embrittlement and cracking which result from the simultaneous application of tensile and compressive stresses and corrosive media. The corrosion-fatigue limit of a metal is the highest stress which it will endure indefinitely (that is, for at least ten million cycles of stress), when subjected to repeated stresses and exposed simultaneously to a corrosive medium. Although air may be considered a corrosive medium, since in some cases at least its exclusion leads to higher corrosive-fatigue values,[73] most studies of corrosion-fatigue have been conducted in water and aqueous solutions.

The observation that the corrosion-fatigue limit of a steel exposed to salt water is lower than that of a steel exposed to fresh water containing a high content of carbonate led to the conclusion that the film-forming characteristics of the latter were related to the result. A somewhat similar improvement in corrosion-fatigue resistance was obtained by the introduction of chromium, a film-forming substance, into steel. In view of these results the use of protective metallic coatings for the prevention of corrosion-fatigue suggested itself. Tests employing cadmium coatings were favorable, and these led to a study of the protective value of zinc coatings for this purpose.

Zinc coatings were applied to a fairly hard steel in the form of round rods by hot-dipping, sherardizing and electroplating, and these specimens were employed in a rotating beam type fatigue machine to investigate the protective action of zinc against the corrosion fatigue of steel in a moderately hard water.[74] The machine was operated at 1750 r.p.m., and the test carried out in a temperature range of 65 to 76° F. The results of the test on these specimens were as follows:

Material	Fatigue Limit (lbs./in.^{2})
Bare steel	20,000
Hot-dipped zinc coating	43,500
Sherardized zinc coating	43,500
Electroplated zinc coating	60,500

Toxic Properties of Zinc

There is some uncertainty concerning the toxic properties of zinc despite the fact that much has been written on the subject. Zinc is found normally in plant and animal tissues and is known to be excreted by the body. The conclusion seems warranted, however, that consumption of zinc beyond a small amount which may be necessary for the proper functioning of the animal system may give rise to toxic effects. The U. S. Public Health Service has placed a maximum safe limit on the zinc content for culinary and drinking water supplied by common carriers at 5 milligrams per liter.[75] This limit is considered conservative by other investigators [76] who, from a review of the literature and their own experiments, conclude that 40 milligrams of zinc per liter of water is safe for human consumption. It has been pointed out, for example, that water from galvanized storage tanks containing 17.1 parts per million supplied for drinking purposes at Brisbane, Australia, caused no observably harmful results.

---

[72] McAdam, D. J. Jr., *Pro. Am. Soc. Testing Materials*, **26**, Pt. 2, 224 (1926).

[73] Gough, H. J., and Sopwith, D. G., *J. Inst. Metals*, **56**, 55 (1935).

[74] Harvey, W. E., *Metals and Alloys*, **1**, 458 (1929-30).

The zinc content of ground waters flowing through galvanized pipe is commonly from 5 to 15 parts per million.[77] As previously stated in this chapter, soft waters and waters containing carbon dioxide attack zinc more rapidly than do hard waters. The percentage of zinc actually present in tap water in any given case depends also, of course, upon the length of the galvanized section through which it has passed and the length of time it has stood in this pipe.

It has been contended that chlorination of water increases its corrosiveness toward zinc.[78] Recent studies have shown, however, that water containing 5 parts per million of chlorine produces less attack on galvanized iron than does distilled water.[76]

It is generally recognized that zinc-coated dishes are unsuitable for use in the preparation of foods, particularly acid foods. The use of zinc-coated containers, pails, tubs and the like in making lemonade and similar drinks, which used to be not infrequent for large gatherings, is especially to be guarded against. An investigation by the Bureau of Chemistry of root beer which was suspected of being the cause of numerous cases of slight poisoning indicated that the beverage contained 229 milligrams of zinc per liter. Tests made to show the rate at which various liquids would dissolve zinc when allowed to stand in a zinc-coated pail gave the results summarized in Table 12.[79]

Table 12.—Zinc Dissolved from Zinc-Coated Iron Pails.

Liquid	Zinc, mg/liter after 17 hours	Zinc, mg/liter after 41 hours
Tap Water (Washington, D. C.)	5	21
Distilled Water	9	27
Carbonated Water	193	181
Milk	483	1054
Orangeade	540	854
Lemonade	1411	2700

---

[75] U. S. Public Health Service Reprint 1029, page 693, Public Health Reports, April 10, 1925.

[76] Anderson, E. A., Reinhard, C. E., and Hammel, W. D., *J. Am. Water Works Assoc.*, **26**, 49 (1934).

[77] Howard, C. D., *J. Am. Water Works Assoc.*, **10**, 411 (1923).

[78] Lothian and Ward, *J. Roy. Army Med. Corps*, **39**, 169 (1922).

[79] Sale, J. W., and Badger, C. H., *J. Ind. and Eng. Chem.*, **16**, 164 (1924).

Chapter 7

Cadmium Coatings and Their Protective Value

The importance assumed by cadmium coatings in recent years may be attributed to the pleasing appearance of the metal and the fact that, indoors at least, it furnishes satisfactory protection against rusting. Although somewhat similar to zinc in its properties, cadmium darkens less readily and usually does not develop corrosion products of a bulky and loose nature. Owing to the high cost of cadmium which has increased in recent years, it has not attained very widespread use. Since, as will be shown later, its efficacy as a protective coating is in general inferior to that of zinc, interest in cadmium as a coating material has waned of late. In actual volume of plating, however, cadmium coatings increased over the period 1929 to 1936 largely as a result of its adoption for certain applications such as electrical contacts, radio apparatus, washing machines, etc.[1]

Cadmium, like zinc, is electronegative or anodic to iron and protects exposed areas of an iron surface by sacrificing itself.[2] The potential difference between cadmium and iron is less than that between zinc and iron, and for this reason cadmium does not in general cathodically protect as large an area of exposed iron as does zinc. Indeed it is possible that in some environments the potentials of cadmium and iron may be reversed. permitting "pinhole" corrosion of iron through pores in the cadmium coating.

METHOD OF APPLICATION OF CADMIUM COATINGS

Cadmium coatings are applied on a commercial scale only by electroplating. Some effort has been made to produce coatings by hot dipping[3] and also by metal spraying, but neither method has attained much importance. Sprayed cadmium coatings are said to be used abroad, however, on propeller shafts, Diesel engine walls and buoys in contact with sea water.[4] The first patent on the electrodeposition of cadmium was issued in England in 1841; the process was in successful but limited operation shortly thereafter. Not until about fifteen years ago, however, was the metal electroplated on a commercial scale as a protective coating. It is of interest to note that the solution first used for cadmium plating—cadmium carbonate dissolved in a solution of sodium cyanide—is of the same general nature as those used in commercial cadmium plating at the present time.

---

[1] Soderberg, K. G., *Monthly Rev. Am. Electroplaters Soc.*, 23, 33 (Nov., 1936).

[2] Rawdon, H. S., *Trans. Am. Electrochem. Soc.*, 49, 339 (1926).

[3] Siemens, A., *Met. Ind. (London)*, 36, 481 (1930); *see also*, DeLattre, *Rev. met.*, 25, 630 (1928).

[4] Humann, *Werft, Ruderer and Hafen*, 16, 40 (1935).

Modern cadmium plating solutions are prepared by dissolving cadmium cyanide or cadmium oxide in sodium cyanide, obtaining the double cyanide of cadmium and sodium, $NaCd(CN)_3$ and usually some "free cyanide." The cadmium content of the bath may vary from 0.25 to $0.8N$, *i.e.,* from 15 to 30 grams per liter, and the free sodium cyanide from 0.15 to $0.6N$, *i.e.,* from 7.5 to 30 grams per liter.[5] A typical cadmium plating bath may contain $0.35N$ CdO (23 grams per liter), $1.5N$ sodium cyanide (75 grams per liter), and $0.4N$ sodium hydroxide (15 grams per liter). Addition agents, for example, gulac, which is a waste product of the sulfite pulp industry, may be employed to improve the character of deposit.[6] The use of a very small percentage of nickel in the cadmium bath produces a bright deposit.[7]

The plating solution is operated at ordinary room temperature and in the current density range of 1 to 5 amperes per square decimeter (9 to 47 amperes per sq. ft.)[5] Cadmium anodes may be successfully used. Owing to the tendency in some baths toward anode corrosion it has been recommended that stainless steel be used to replace up to 75 per cent of the anode area.[8]

Cadmium plating baths contain the complex cadmium-cyanide radical $[Cd(CN)_3]^-$ an analog of the complex zinc ion $[Zn(CN)_4]^{--}$. As in the case of cyanide-zinc solutions, the cadmium cyanide bath, owing to the low degree of dissociation of this complex ion, maintains a very low metal ion concentration, and consequently has a high throwing power. It is well known that cadmium baths produce coatings of a good degree of uniformity on parts of irregular shape.

Zinc-cadmium alloys may be readily deposited from cyanide solutions containing the two metals. It is usually difficult to control the composition of the deposit, the variation in cadmium content running from about 4.5 to 15 per cent. These alloy coatings are initially somewhat brighter than zinc in appearance, but become mottled and unsightly upon short exposure out of doors.[9]

Protective Value of Cadmium Coatings

There was for several years considerable controversy as to the value of cadmium coatings for the protection of iron and steel and particularly as to their relative efficacy as compared with zinc coatings.[10] Much of the interest in cadmium coatings arose from their favorable showing in the salt spray test at a time when greater credence was given to the dependability and significance of accelerated tests. With the decline of faith in accelerated testing it continued to be argued that the salt spray test in simulating marine atmospheres gives a reliable estimation of the relative behavior of materials to be used in seaside localities and aboard ocean-going ships. While there is some merit in this contention, more recent atmospheric exposure tests have shown that even in marine locations cadmium is inferior to zinc. Cadmium does, however, resist attack in these locations markedly better than it does in industrial atmospheres. Contrary to the behavior of zinc coatings it is found that cadmium plate is somewhat more severely attacked in a marine exposure in the tropical zone than in a similar location in the temperate zone.

---

[5] Blum and Hogaboom, "Principles of Electroplating and Electroforming," 2nd ed., p. 334, New York, McGraw-Hill Book Co., 1930.

[6] Blum, W., Strausser, P. W. C., and Brenner, A., *Bur. Standards J. Res.* **16,** 185 (1936).

[7] Westbrook, L. *Trans. Am. Electrochem. Soc.* **55,** 333 (1929).

[8] Wernick S., *Trans. Electrochem. Soc.,* 60, 117 (1931).

[9] Hippensteel, C. L., and Borgmann, C., *Trans. Am. Electrochem. Soc.,* **58,** 23 (1930).

[10] Gillett, H. W., *Metals and Alloys,* **1,** 667 (1929-30).

The joint atmospheric corrosion test on electroplated coatings being conducted through the coöperation of the American Electroplaters' Society and the American Society for Testing Materials with the National Bureau of Standards has included a study of cadmium coatings.[6] This test has been mentioned previously and the results obtained for zinc coatings are given in Table 7 in Chapter 6. The results obtained for cadmium coatings in this test at the end of an exposure of about 180 weeks are given in Table 13. It will be recalled that a system of rating quality, in which more importance was attached to the early stages of rusting, was devised for

Table 13.—Quality Ratings and Per Cent of Surface Rusted for Cadmium Coatings. 180 Weeks' Exposure to Atmosphere.[6]

Description of Plating Bath	Thickness mils (in.×10^3)	New York		Pittsburgh		Sandy Hook	
		T %	R %	T %	R %	T %	R %
Standard	0.2	16	75	17	75	43	75
Cyanide	.5	26	75	43	75	94	3
	1.0	44	75	81	65	94	0
Cyanide with gulac.	.2	16	75	17	75	47	75
	.5	27	75	37	75	88	3
	1.0	46	75	71	75	96	0
Cyanide with gulac. and nickel	.2	14	75	18	75	46	75
	.5	28	75	34	75	90	6
	1.0	44	75	81	75	97	0

		Key West		State College		Washington	
		T %	R %	T %	R %	T %	R %
Standard	0.2	81	..	94	4	59	75
Cyanide	.5	81	..	100	0	97	3
	1.0	81	..	100	1	96	2
Cyanide with gulac.	.2	81	..	85	8	58	75
	.5	81	..	100	0	97	2
	1.0	81	..	100	0	100	0
Cyanide with gulac. and nickel	.2	81	..	87	8	78	75
	.5	82	..	100	0	96	2
	1.0	82	..	100	0	99	1

evaluation of the results. This quality rating over the period of test is expressed in the table as (T), and per cent of surface rusted at the end of the test as (R).

Comparison of the results in this table with those recorded in Table 7 for coatings of zinc exposed at the same test stations shows that without a single exception the quality ratings of the cadmium coatings are lower than those for zinc coatings of similar thickness. The comparison shows further, as stated above, that the superiority of zinc coatings is somewhat less pronounced in marine locations than in industrial, urban and rural exposures.

Cadmium and zinc coatings have been compared in performance in the extensive atmospheric exposure program of tests being carried out by the American Society for Testing Materials. The comparative behavior of the two coatings plated on steel plates and zinc-dipped corrugated sheets obtained in this test over a period of nine years at Brunot Island, Pittsburgh is shown graphically in Figure 27.[11] The progressive development of rust on cadmium and zinc-coated hardware specimens for a shorter period at the same location is given in Figure 28.

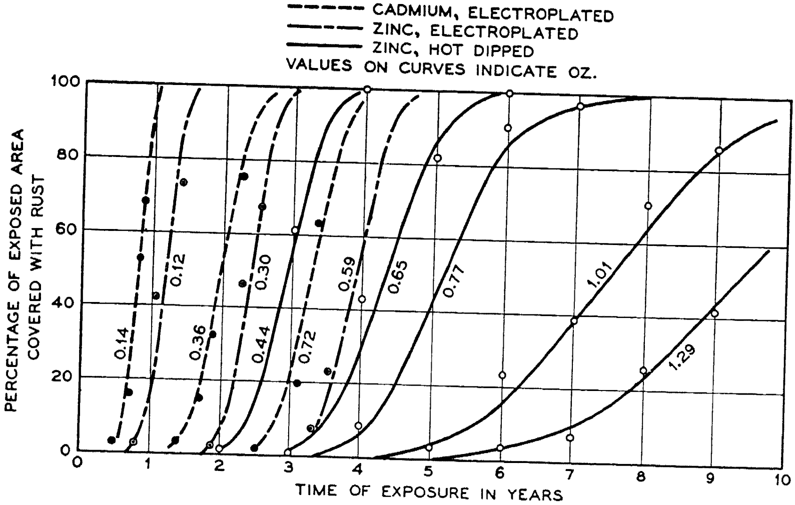


Figure 27.—Progressive Development of Rust at Brunot Island (Pittsburgh, Pa.) on 4- by 6-in. Steel Specimens Plated with Cadmium and Zinc and on Corrugated Galvanized Sheets.

These tests likewise demonstrate the marked inferiority of cadmium coatings in an industrial atmosphere. It is of interest to note that the protection afforded to steel by cadmium coatings is proportional to the thickness of the coating, as has been well established for zinc coatings.

---

[11] Passano, R. F., *Proc. Am. Soc. Testing Materials,* **36,** pt. I, 107 (1936).

The more rapid corrosion of zinc coatings in industrial atmospheres has been attributed to their inability to develop, in such exposures, films of corrosion products which are basic in character and of low solubility. It would appear from the behavior of cadmium coatings in similar atmospheres that the surface films must be of even higher solubility than in the case of zinc. While the composition of corrosion products is usually complex and variable, those forming in industrial atmospheres generally contain sulfates, and it may be significant in this connection that cadmium sulfate is nearly twice as soluble as zinc sulfate. It is generally recognized that the lower solubility of cadmium chloride as compared with zinc chloride accounts for the greater resistance of cadmium coatings in the salt spray test. Inasmuch as this superiority of cadmium in salt spray is not realized in outdoor marine exposures it is evident that the corrosion products formed in such localities are probably not merely the chlorides of the metals.

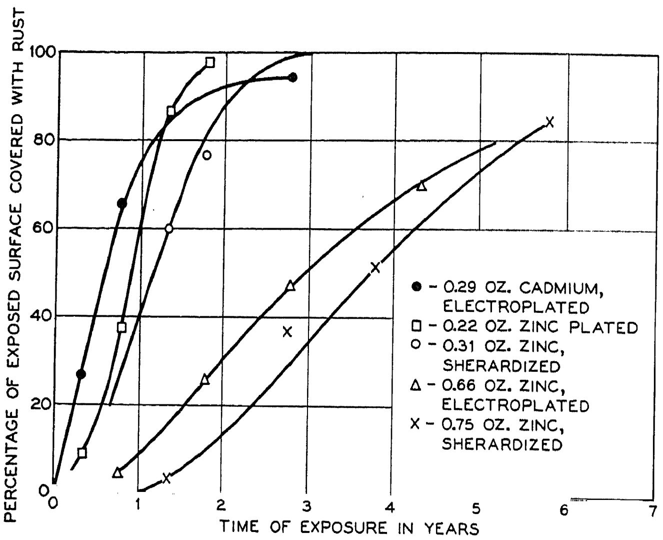


Figure 28.—Progressive Development of Rust at Brunot Island (Pittsburgh, Pa.) on Hardware Specimens Coated with Zinc and Cadmium.

The effect of spraying cadmium coatings with water, thereby simulating increased rainfall, does not increase the rate of corrosion of cadmium in New York City atmosphere. See Figure 22 in Chapter 6 for a comparison of zinc and cadmium coatings as influenced by water spraying. Apparently the natural rainfall which occurs at this test station is sufficient for the dissolution of the cadmium corrosion products, but inadequate for the removal of the film forming on zinc.

The favorable performance of cadmium coatings in indoor service may be attributed to the fact that in air of moderate humidity films of protective character tend to form. For example, it has been observed that cadmium coatings under such conditions gain weight with time of exposure in accordance with a roughly parabolic law.[12] This suggests that the progress of the reaction is controlled by the rate of diffusion of oxygen or other corroding elements through the increasingly thicker film of corrosion products. In contrast to this it will be recalled that the film formed on zinc under such conditions is of such nature as not to retard corrosion.

Under conditions of higher humidity indoors the corrosion products of cadmium coatings become deliquescent, with the result that the rate of attack is accelerated. There is evidence that the relative humidity at which cadmium corrosion products become deliquescent is markedly lower than it is for the corrosion products of zinc.[12] This tendency of cadmium to develop a film of moist material on its surface at relative humidities well below the dew point may be a factor accelerating the corrosion of cadmium coatings outdoors.

Finally it may be of interest to note that the relative rates of corrosion of cadmium and zinc are of the same general order as their equivalent weights, 56 and 33 respectively.

[12] Patterson, W. S., *J. Electroplaters and Depositors Tech. Soc.,* 5, 91 (1930).

Chapter 8

Tin Coatings

Tin-plate combines in a single material the relatively superior corrosion resistance of a non-ferrous metal with the strength of steel. Tinned sheet metal can be severely deformed without serious damage to the coating; consequently rather complicated articles are produced by stamping, drawing, rolling, bending, curling, and lock-seaming. Tin is in many respects an excellent coating metal. It can be applied as an extremely thin and reasonably uniform coating over the surface and is resistant to atmospheric corrosive attack and to aqueous solutions in the absence of oxygen. Since tin lends itself admirably to soldering operations and has no toxic effect upon foodstuffs in contact with it, tin-plate is used in great quantities in the canning industry. Indeed it may be said that the canning industry, which is so important a feature of modern life, is based upon the suitability of tin-plate as containers for the preservation of foods. In 1935 approximately 59 per cent of the domestic consumption of tin-plate was used in canning, all other applications using but 41 per cent of the million and a half tons of tin-plate consumed in this country in that year.[1]

The annual world consumption of tin-plate would be sufficient to supply a band of this material 100 feet wide and long enough to girdle the earth at the equator, and the tin used annually in solders (if alloyed with 50 per cent lead) would provide 250 soldered seams to parallel this equatorial band.[2] About 40 per cent of the world production of tin goes into tin-plate.

In addition to its use in the form of tin-plate, tin is employed to a much lesser extent in coating copper. Among the applications of tinned copper are roofing material, cooking utensils and refrigeration equipment. In the electrical industry tinned copper wire is used in considerable quantity.

Tin coatings have been applied almost exclusively by hot-dipping until recently, and the term "tin-plate" for tin-coated steel has been associated with the dipping process. In recent years electrodeposited coatings have assumed greater importance and this trend may be expected to continue, owing to the development of processes for continuous electroplating of steel strip. The application of tin coatings by wiping fused tin over the surface to be coated is restricted to copper. Tin coatings may be applied readily by the metal-spraying process. By spraying thick coatings or by scratch-brushing successive layers of sprayed tin the porosity characteristic of this type of coating may be diminished. Recently it has been shown that tin coatings may be deposited from the vapor phase by decomposition of stannous chloride vapor in a hydrogen atmosphere.[3] This process which has been called "stannising," has been applied so far only in an experimental way and principally to copper. The coating consists of an alloy of tin and the basis metal.

---

[1] Statistical Yearbook (1937) *Internat. Tin Research and Dev. Council.*

[2] Macnaughton, D. J., *Address,* Amer. Inst. Min. and Met. Eng., New York, Feb. 21, 1935. Published by International Tin Research and Development Council, No. 5, October, 1935.

HOT-DIPPED TIN COATINGS

Historical

Metallic tin has been used for many centuries. As early as 1500 B. C. the Phoenicians were obtaining tin from Cornwall for use in making bronze. The coating of copper vessels with tin was known to the Romans as was the tinning of cast-iron cooking utensils which were mentioned by Pliny as existing before 23 A. D.[4] There is evidence [5] that the coatings were applied by immersion in a bath of molten tin. It is reasonable to believe, however, that the much simpler process of tinning by applying the metal to the surface of the heated article was also employed by the ancients.

Coating sheet iron with tin is of much more recent origin. According to legend a Cornish tin miner discovered tin in the Erzgebirge mountains of Bohemia about 1240 A. D.[6] The tin-plate industry seems to have become well established in Bohemia between this date and 1575 A. D. when it is recorded that block tin was imported from Cornwall for the manufacture of tin-plate, the local supply apparently being insufficient to meet the increasing demand. About 1600 the manufacture of tinned iron sheets was begun in Saxony, and by 1665 Dresden had become a flourishing center for the production of this material. It is said that the secret of the art was stolen for the Duke of Saxony by a monk who visited Bohemia in disguise.

The introduction of tin-plate manufacturing into England was the result of the efforts of Andrew Yarranton who, during a depression of the metal industry in England, particularly relating to tin and iron, visited Dresden for the express purpose of becoming familiar with the manufacture of tin-plate. Accompanying Yarranton, according to his well-known book, *England's Improvement by Sea and Land,* was a man "that well understood the whole nature of iron." The party was well received in Dresden and no efforts were made to conceal any of the operations. Upon returning to England with the information sought, Yarranton made preparations for starting the industry at Pontypool in southwestern England. The establishment of the industry was a slow process, for although Yarranton applied himself to "setting this beneficial thing to work" his efforts failed owing to the granting of a patent for the process to a rival who had influence at court. In 1697 Houghton reported that there were no tin-plate works in Great Britain. Not until 1720 when Hanbury took up the project again at Pontypool was the tin-plate industry in England definitely established. Once started, the industry grew rapidly, especially after a method for producing the iron sheets by rolling instead of hammering them by hand was developed in 1728. The South Wales district became the center for the production of practically all of the world's supply of tin-plate, a position which it retained until late in the 19th century. The abundance of iron ore, wood for charcoal and the discovery of pit coal in 1870 made this region a particularly favorable one for the industry.

---

[3] Gonser, B. W., and Slowter, E. E., *Internat. Tin Research and Dev. Council, Tech. Pub. (A)* No. 76, April, 1938.

[4] Flower, P. W., "History of Tin and Tin-Plate," London, G. Bell & Sons, 1880; *J. Iron Steel Inst.,* No. 1, p. 36 (1886).

[5] Goodale, "Chronology of Iron and Steel," Pittsburgh Iron and Steel Foundries Co., 1920.

[6] Macnaughton, D. J., and Hedges, E. S., *Internat. Tin. Res. and Dev. Council,* Bull. No. 1, Feb., 1935. This bulletin has been drawn upon for historical aspects of the tin-plate industry.

The manufacture of tin-plate in the United States was begun about 1891 following the enactment of the McKinley tariff which imposed a duty of 2.2 cents per pound on tin-plate. In recent years this country has become the largest producer of tin-plate, accounting in 1935 for 53.8 per cent of the world's output. There are 17 companies operating 28 plants with a total annual capacity of 2,574,000 long tons of tin-plate. Nearly 99 per cent of the tin-plate produced in the United States is of the type known as "coke" tin-plate containing approximately 35 pounds of tin per long ton of product, in contrast to the heavier coated variety known as "charcoal" tin-plate.

Outline of the Process

As in the analogous case of zinc coating, the application of a tin coating to a material such as steel sheet constitutes only a small part of the total work required in preparing such material. Although there are characteristic differences in preparing the sheets in the zinc coating and tin coating industries, the essentials are the same.

Following the introduction of rolling mill technique, iron sheet was used for tinning until about 1870 when it was gradually displaced by Bessemer steel. It was early found advantageous to roll the sheets in packs. This is accomplished by hot rolling bars of steel to the finished gauge by preheating, rolling, and doubling until a pack of eight sheets is produced uniform in substance and of correct gauge.[6] It is more common practice at present to cut the hot-rolled steel at an early stage into a large number of small bars which are then rolled to the final thickness. With the development of the process of continuous rolling of steel strip, the older methods of producing sheet stock for tin-plate are being superseded. In the United States, steel ingots weighing several tons are rolled to tin-plate gauge, producing strip which may be 5000 feet in length and 3 feet in width. While strip 10 inches in width is being tinned continuously on a commercial scale, the present practice is to cut the wider strip into relatively short lengths for the tinning operation.[7]

The hot-rolled sheets are carefully cleaned by acid pickling. This process is carried out in two stages: the first, which is termed "black pickling" is accomplished by immersing the black sheets in sulfuric acid (approximately 6- to 12-per cent) which is kept hot with steam. After the annealing, cold rolling and second annealing operations which follow the first pickling, the sheets are given the "white pickling" in dilute sulfuric acid (2- to 6-per cent), and after washing are ready for the tinning operation.

---

[7] Macnaughton, D. J., Tait, W. H., and Bair, S., *J. Electrodepositors' Tech. Soc.*, 12, 45 (1937).

Hand Dipping

The old process for making tin-plate by hand dipping is of interest. The sheets were cleaned by scouring with sand and water and by being immersed in sour barley water for several days. The use of sulfuric acid for pickling dates only from the early part of the nineteenth century. The sheets, after being cleaned, were immersed in a bath of hot grease before immersion in the molten tin. Tallow, which was used in the early days and is used to a limited extent today in hand dipping, was replaced later by palm oil which is still widely used for this purpose. From the grease pot the sheets were lowered one by one into the molten tin which was kept covered with a thick layer of the grease in order to prevent oxidation. Upon removal from the first tin bath, the sheets were brushed with a hemp brush and immersed in a second tin bath usually of somewhat higher purity and maintained at a somewhat lower temperature than the first, and finally in a third tin bath of highest purity. Close regulation of the amount of tin carried by the sheet was not possible although the workmen became very adept in obtaining very uniform distribution of the coating over the surface of the sheet. After the coating had solidified, the sheets were rubbed free from most of the oil by means of bran or a similar substance and then "dusted" with a sheep fleece to give a high luster. Sheets coated in this manner always had a very heavy coating as compared with the present commercial "coke" plate.

The present hand-dipping method for tinning small irregularly shaped castings and for tinning articles cut or manufactured from tin-plate or plain "black" sheet steel, such as kitchen utensils, does not differ essentially from the old hand-dipping method. The retinning of articles is also done in essentially the same manner. Considerable difficulty is often experienced in tinning castings by hand dipping, primarily on account of an improperly cleaned surface. The first cleaning is often done with hydrofluoric acid, and sometimes sand blasting is employed. After this, the casting is pickled and the resulting film of graphite must then be carefully rubbed off. Following this, a treatment with a copper solution to give a film of precipitated copper is often recommended.[8] The article is then immersed in the molten tin, the flux commonly used being zinc chloride. Iron castings which have been given an annealing treatment somewhat akin to the treatment used for producing malleable castings, so that surface decarbonization has been brought about, can be tinned, as a rule, very much more readily than ordinary castings.

---

[8] Schott, E. A., *Stahl Eisen*, **39**, 119 (1919); *Marnoch, Giesserei*, **37**, 691 (1926); *Iron Age*, **118**, 1318 (1926).

Mechanical Dipping

A marked advance in the tinning process was the invention, about 1863, by Morewood and, independently, by Saunders and Piper, of a device for passing the sheets as they came from the bath through a set of rolls located in the oil layer above the tin. The rolls worked rather closely against each other so that the molten tin was distributed uniformly over the surface.

The use of zinc chloride as a flux for treating the sheets prior to immersion in the tin accompanied and, to some extent, made possible the use of the single bath of tin instead of the several separate baths used in the early days. The single-bath method is used today almost exclusively for tinning when carried out mechanically, although the bath is usually divided into two compartments. Figure 29 is a section of a tinning pot used early in the industry and shows the arrangement of the essential features, flux, molten tin bath, palm-oil layer and rolls. The sheets, after being cleaned, were fed by hand one at a time through the flux into the tin and then raised vertically by the lever so as to be caught by the rolls and carried upward and out of the pot. This method in principle is still used, though to a very

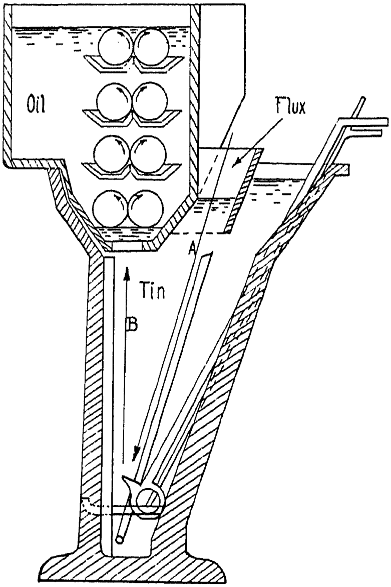


Figure 29.—Early Form of Tinning Machine. The arrows indicate how the sheet is passed through the tin and oil baths. The pans beneath the exit rolls contain molten tin to aid in forming uniform and heavy coatings. [Harbord, F. W., and Hall, J. W., "Metallurgy of Steel," 7th ed., Philadelphia, J. B. Lippincott Co., 1923.]

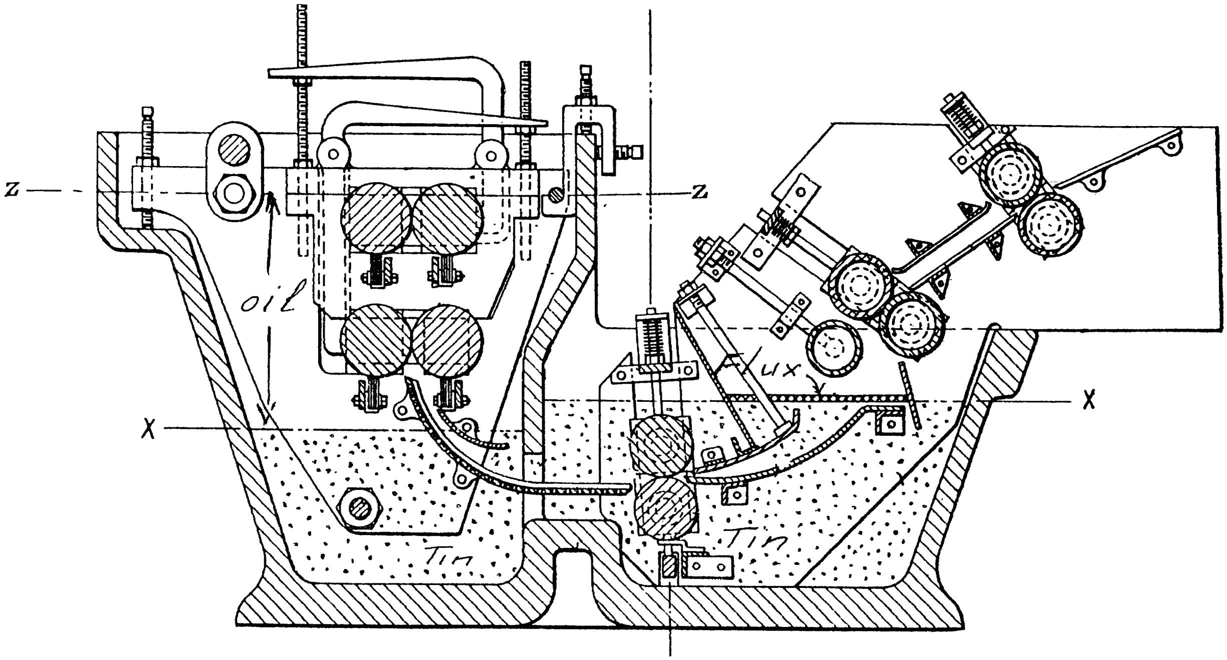


Figure 30.—Section of "Tin Pot" of a Modern Tinning Machine.[10]

limited extent,[9] for the production of heavily coated tin-plate. It is not suitable for very long sheets which are apt to buckle and bend when raised from the lower edge, nor is the method a rapid one.

Figure 30 shows a section of a tin pot in current use for the mechanical tinning of the grade of tin-plate commonly termed "coke-plate."[10] Such a pot contains from 5000 to 10,000 pounds of tin.

After being cleaned the sheets are passed through the zinc chloride flux layer into the molten tin by means of the rolls and guides at the right. The molten metal in the first compartment of the cast-iron container is generally kept at a somewhat higher temperature than that in the second. The machine is usually wide enough to permit two or more sheets to pass through side by side simultaneously. The sheet is guided through the tin bath by the curved guides shown, and by means of the rolls is passed upward through the oil layer. The oil keeps the tin coating on the sheet molten long enough to aid in obtaining a layer as uniform in thickness as possible. It also aids in giving luster by preventing any superficial surface oxidation.

The machine process as just described is not employed for the production of heavily coated tin-plate ("charcoal plate") except perhaps for rather light-gauge sheets. For charcoal plate, a "combination pot" is often used. In this process the sheet is first dipped mechanically in a manner analogous to that described above, after which it is dipped by hand in a pot of pure tin maintained at a rather low temperature, then passed between rolls in the palm-oil bath, whereby the relatively heavy coating of tin is uniformly distributed over the surface.

The tin-coated sheets always carry with them a film of oil as they leave the oil bath. The greater part of this must be removed by a hot alkaline wash and by rubbing with some substance such as bran or middlings. The sheets are then clean and have a high luster. All grades of commercial tin-plate retain some oil on the surface. This serves a useful purpose, however, in retarding the initial corrosion of the sheet, especially during storage and shipment. Such a residual film of oil is not sufficient to be harmful to such operations as lacquering and printing.

Aside from copper wire very little wire is tinned. The process is carried out in a manner quite similar to the zinc-coating of wire.

The tin used in the manufacture of tin-plate is of high grade and no attempt is made to use any additions of metallic ingredients as is not infrequently done in the zinc coating industry. The addition of aluminum, for example, would be expected to be detrimental since sheet tin containing small proportions of aluminum becomes brittle on the surface[11] and may even become so brittle as a result of corrosive attack[12] that it can be broken up into tiny fragments by the fingers. Small percentages of iron, lead, arsenic or antimony are said to decrease the luster of tin and to impart to it a yellowish color.[13] The presence of several per cent of zinc in a tin coating is reported to improve its corrosion resistance, and the addition of iron to the extent of 0.5 to 1.5 per cent increases hardness and wear resistance.[14] The transformation of ordinary tin into its powdery grey allotropic form, which is accelerated at low temperatures, is a rare occurrence although it is said to have been observed on the surface of tinned iron.[15] It may be prevented by the addition of 0.5 per cent of bismuth. Bismuth in proportions up to 10 per cent increases the whiteness and brightness of tin coatings. All such additions, however, if used at all, are for very special products and not for commercial tin-plate.

---

[9] Poppleton, C. F., *Iron Age*, **101**, 30, 127 (1918); Camp, J. M., and Francis, C. B., "The Making, Shaping and Treating of Steel," 4th ed., p. 983, Carnegie Steel Company, Pittsburgh, Pa., 1925.

[10] Davis, S. A., U. S. Patent 1,528,407.

[11] Hanson, D., and Sandford, E. J., *J. Inst. Metals*, **56**, 191 (1935).

[12] Heyn, E., and Wetzel, E., *Mitt. Kaiser Wilhelm Inst., Metallforschung*, **1**, 4 (1922).

Ordinarily the "spangle" effect which is so pronounced in zinc coatings is entirely lacking in tin coatings. The crystalline pattern of tin coating can be readily developed by dipping the coated article in dilute hydrochloric acid and this is sometimes done for ornamental effects. Such an etch-pattern is often very pronounced on the inner surface of tin cans in which certain food products have been preserved.

Operating Conditions of Molten Tin Bath

Temperature control of the tin bath is of considerable importance. The usual working temperature of the tin bath is from 600 to 625° F. (315 to 330° C.) while that of the palm-oil layer is 455 to 480° F. (235-249°C.).[16] When the bath consists of two compartments the temperature of the tin in the first one is maintained considerably higher than in the second. For example, a suitable temperature for the tin in the first compartment is 600° F. (315° C.) and in the second 550° F. (288° C.). The need for the somewhat lower temperature in the second compartment arises from the fact that here the palm oil comes in direct contact with the molten tin. If the temperature is too high the oil polymerizes and no longer serves to keep the tin clean. Studies of possible substitutes for palm oil have shown that hydrogenated cotton-seed oil, which does not polymerize, is satisfactory in performance.[17] The consumption of this oil was distinctly less than that of palm oil in a commercial test, although the hardened oil is more expensive. It is understood that hardened whale oil has been found in Germany to be a satisfactory substitute.

The speed at which the sheet is passed through the molten tin in commercial practice is an important factor in determining the amount of tin used in coating a unit area of sheet, or the "tin yield" as it is known in the mill. Formerly a speed of 100 to 120 inches per minute through the tin pot was considered the maximum to be used in tinning coke plate.[10] At present hot-tinning of steel is frequently conducted at speeds up to 300 inches per minute.[7] Increase in speed of the rolls tends to increase the thickness of coating up to peripheral speeds of 250 inches per minute. Increasing the pressure of the rolls decreases the weight of the tin coating, as would be expected.[18]

---

[13] Mantell, C., *Mining & Met.*, 10, 90 (1929).

[14] Maass, E., *Korr, u. Metallschutz.*, 1, 124 (1925).

[15] Hasslinger, R. v., *Sitzb. Akad. Wein.*, 117, 501 (1908).

[16] Collins, W. D., and Clarke, W. F., *J. Ind. Eng. Chem.*, 12, 149 (1920); Williams, I., Paper presented Jan. 23, 1932, Metallurgical Soc., Swansea Tech. College.

[17] Collins, W. D., and Clarke, W. F., *J. Ind. Eng. Chem.*, 12, 149 (1920).

The thickness of a tin coating is also dependent upon the character of the surface of the sheet, particularly its condition with respect to the degree of pickling received. A sheet roughened by over "pickling" takes on considerably more tin than does a properly pickled sheet, and it is also more difficult to impart a satisfactory luster to such sheets. The adjustment of the exit rolls, that is, their grip on the sheet, is an important factor in determining the uniformity of the coating. As would be expected the hardness or surface condition of the rolls has a definite bearing on the weight of coating; re-tinning or "mending," on the other hand, is without influence.[18]

Structure of Hot-Dipped Tin Coatings

Hot-tinning of iron or copper depends upon the fact that the surfaces of these metals may be wetted by molten tin, just as iron is wetted by molten zinc in the analogous operation of zinc-dipping. In general, it may be said that metals wet other metals with which they form compounds or solid solutions.[19] Tin forms intermetallic compounds with both iron and copper, but it does not appear to form a solid solution with iron at the tin-rich end of the diagram, which is the region of interest in tin-plate.[20] These compounds, $FeSn_2$ in the case of tinned iron, and Cu_6Sn_5 and Cu_3Sn when copper is the coated metal, crystallize out as the coatings are formed. The formation and growth of these interfacial compounds are governed by diffusion of the reactants through the compound layers. While there is still some uncertainty as to the constitutional diagram of the iron-tin system, there is evidence of two compounds other than $FeSn_2$.[21] These are Fe_2Sn and $FeSn$.

The thickness of the coating on tin-plate is of the order of 1 to 2.5 pounds per base box,[*] for ordinary coke plate. This corresponds to a thickness range of from 59 to 148 millionths of an inch. The layer of tin-iron compound in such coatings has been found to be approximately 0.00002 inch in thickness.[21a] Although the percentage of alloyed tin will vary somewhat depending upon the operating conditions of the bath, it may be assumed to comprise from 10 to 25 per cent of normal coatings ranging from 1 to 3 pounds per base box.

---

[18] Williams, I., Paper presented Jan. 23, 1932, Metallurgical Soc., Swansea Tech. College.

[19] Daniels, E. J., *Trans. Faraday Soc.*, 31, 1277 (1935).

[20] Hoare, W. E., *Proc. Swansea Tech. College Met. Soc.*, page 1, 1934.

[21] Jones, W. D., and Hoare, W. E., *J. Iron and Steel Inst.*, 129, No. 1, 273 (1934).

[*] As will be explained on page 140 the commercial term "base box" (or "basis box" in England) is weight of coating on 31,360 square inches of sheet or 62,720 square inches of surface to be coated.

[21a] Hoare, W. E., *J. Iron and Steel Inst.*, 129, 253 (1934).

The compound $FeSn_2$, containing 80.9 per cent tin, consists of rectangular crystals which may form rapidly at the steel-tin interface at temperatures as low as 150° C. (302° F.), and are stable up to 496° C. (925° F.). These crystals may be seen at the steel-tin interface in Figure 31. Under certain circumstances the compound becomes dispersed in the tin layer as shown in Figure 32.[22] It is not intended to suggest that these pictures are typical of the structures of commercial coatings, although there is some resemblance to them. As previously indicated, when the initial film of compound is formed the subsequent rate of compound formation is

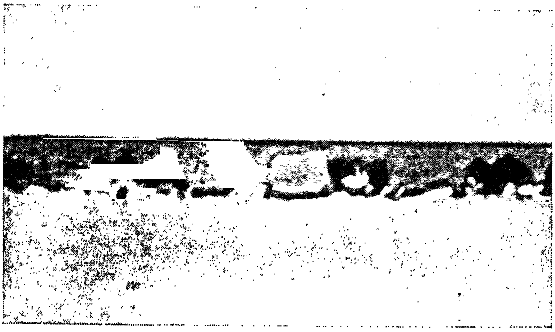


Figure 31.—Hot-Dipped Tin on Steel—Section Showing Alloy Formation. ×500.[22]

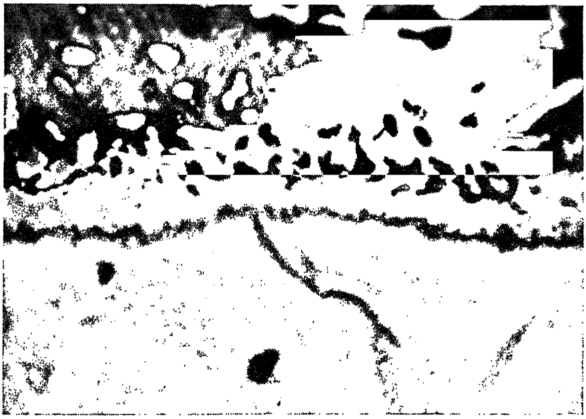


Figure 32.—Hot-Dipped Tin on Copper—Section Showing Alloy Formation. ×1500.[22]

---

[22] Daniels, E. J., and Macnaughton, D. J., "Wetting and Detergency," London, Havey, 1937. Reprinted by Internat. Tin Research and Dev. Council, Series B, No. 6.

markedly curtailed. It is for this reason that the compound layer in tin-plate does not attain thicknesses comparable to those of the iron-zinc compounds in zinc-dipped coatings.

The effect of annealing tin-plates above the melting point of tin is to increase the percentage of alloyed tin.[23] This treatment increases the size of the $FeSn_2$ crystallites.[21]

Tin-plate Commercial Terms

The weight of the coating on tin-plate is expressed as the weight of tin per "base box." The base box is essentially a unit of area, and is the equivalent of 112 sheets, 14 inches by 20 inches, that is, 31,360 square inches of sheet or 62,720 square inches of surface to be coated. For coatings of one pound per base box the thickness of tin is 0.000059 in. The term base box originated in the early days of the industry, and was first used with reference to tin-plate of approximately 30-gauge thickness. A base box of material of this gauge weighs approximately a hundredweight, 112 pounds, a fact which is frequently, but erroneously, embodied in the present-day definition of this term. The manufacture of tin-plate is, of course, not confined to sheets of this size, but a great variety of sizes is made. Some multiple of the original "common standard" size, 10 by 14 inches, still is occasionally used for warehouse stocks and some of the higher-grade products. The weight of the tin coating, however, is always expressed in terms of the base box.

The names "coke" and "charcoal" plate are often used in referring to tin-plate. These terms originated in the early days of the industry when the practice was to use sheets made from ordinary puddled iron for the common grades of tin-plate, and sheets of puddled iron made with charcoal for the higher-grade plate. The original significance of the terms has been entirely lost and, as used at present, they refer in a general way to the weight of tin coating. The coke plate is a cheaper product in that it carries a much lighter coating of tin than does the charcoal plate. The weight of coating of tin on coke plate may vary from 1 to 2.5 pounds per base box and on charcoal plate from 3 to 7 and in Great Britain even up to 14 pounds per base box.

Tin-plate is made in a good many different thicknesses; it is necessary, therefore, that the sheet thickness be specified as well as the weight of coating for any particular grade of material. In designating the thickness or weight of the sheet various trade terms, which originated in the early days of the tin-plate industry, are still used, although many of them have lost most of their original significance.

To meet the varied demands of the present day, tin-plate is made to special order in a good many sizes and gauges. The gauge is usually designated by the weight per base box. The lightest-gauge tin-plate is commonly known as "taggers tin." Much of the coke plate which is used largely in the manufacture of tin cans for the canning industry is made in the larger sizes. There is decided need for simplification in the present system used for commercial designation of tin-plate.

---

[23] Kohman, E. F., and Sanborn, N. H., *Ind. Eng. Chem.*, **19**, 514 (1927).

Tin-plate is used to a very limited extent for roofing. This should not be confused with terne-plate, a widely used roofing material, which is commonly known as "roofing tin."

Electroplated Tin Coatings

One of the most important recent developments in the field of tin coatings is tinning steel strip by electrodeposition. While the process has been largely on a pilot-plant scale until recently, the product is now understood to be available on a commercial basis.[23a] One factor which has retarded the development is the reluctance of the consumers of tin-plate to accept the electroplated product unless its naturally duller appearance is removed by polishing. As a result, a finishing treatment involving scratch-brushing or buffing has been necessary to produce the customary bright surface.

As indicated on a previous page, development of methods for continuous rolling of steel strip bears directly upon the possibilities of utilizing electrotinning as an alternative to hot-tinning. In recent years considerable work has been done also on tin plating baths, with the result that information is available on the technical and economic possibilities of electrodeposited coatings. The relatively thin coating of tin provided by the hot-dipping process is readily obtainable by electroplating methods.

Electroplated tin coatings have been used for buckles, brackets, lamp fittings and other small ornamental articles, as well as for larger pieces like fenders and fire screens for producing an appearance resembling oxidized silver. The electroplating process is used also to a considerable extent to renew the coating on tin-coated articles which are used repeatedly in bakeries, confectionery factories and the like.

Tin Plating Baths

Interest in electrolytic tin refining led some years ago to the development of plating baths from which satisfactory heavy deposits could be obtained. Many types of solution including stannous fluosilicate, acid stannous sulfate, stannous chloride, sodium stannite, and sodium stannate were investigated. Of these types of bath only two, acidified stannous sulfate and alkaline stannate, have proved attractive for the production of tin coatings. The possibilities of wider application of electrodeposited tin coatings have led to considerable study of these solutions.

An alkaline tin bath consisting of stannous chloride in a concentrated aqueous solution of sodium pyrophosphate was used as early as 1850.[7] Later, solutions of stannous chloride in potassium hydroxide were devised and baths of this type, containing an addition agent such as glucose, were employed extensively during the World War. Later it was found that more satisfactory deposits could be obtained from an alkaline stannate bath.

[23a] Thomas, C. G. (Thomas Steel Co., Warren, O.), *Private Communication,* Oct. 27, 1938.

Earlier attempts to use stannate baths resulted in the production of spongy deposits due to the presence of stannite ions which decompose, with the precipitation of metallic tin. Successful operation of stannate baths has been obtained by maintaining tin in the quadrivalent state by means of oxidizing agents. This was accomplished first by periodic additions of hydrogen peroxide or sodium perborate.[24] More recently it has been shown that it is possible by the use of insoluble anodes to maintain tin in the stannate condition without additions of oxidizing agents to the bath.[25] Nickel anodes are used for this purpose at intervals following periodic replenishments of tin furnished by anodic solution. A satisfactory alkaline stannate bath may be obtained by the use of 15 to 20 grams per liter of sodium hydroxide and 85 grams per liter of tin in the form of sodium stannate. This bath is operated at 70-75° C. (158-167° F.) and at current densities from 15 to 20 amperes per square foot. It is possible to use current densities up to about 60 amperes per square foot but with some sacrifice of cathode efficiency.

The development of acid tin plating baths, which is comparatively recent, arose from the demand for electro-refined tin. In these baths, the metal is entirely in the bivalent state. One of the first solutions used in electrorefining consisted of stannous fluosilicate containing hydrofluosilicic acid, and glue as an addition agent. Somewhat later the fluosilicate was replaced by sulfate and hydrofluosilicic acid by cresol-sulfonic acid and this solution, somewhat modified, came to be used in tin plating. The tendency of simple acid sulfate baths to yield feathery deposits and to precipitate basic tin compounds is prevented by the use of suitable addition agents. Recent work has shown that a solution of the following composition may be used to obtain very satisfactory tin coatings:[26] 30 grams of tin (introduced anodically), 50-100 grams of free sulfuric acid, 100 grams of cresol-sulfonic acid, 2 grams of gelatin, and one gram of beta-naphthol per liter of solution. This bath is used at room temperature with a current density of 15-20 amperes per square foot; higher current densities (up to 80 amperes per square foot) may be used if the solution is agitated. The solution has good covering power and excellent throwing power, and it operates at nearly 100 per cent cathode efficiency even at the higher current densities.

Electroplating of Steel Strip

As previously stated, considerable interest has developed in the production of tin-plate by electrodepositing tin on steel strip. Both laboratory and plant studies are being made of the feasibility of the process. Plating baths of both the acid type[27] and the alkaline stannate type are under investigation for this purpose. The use of undercoatings of copper and of hot-dipped tin have been suggested as a means of improving the continuity of the tin coating.

---

[24] Oplinger, F. F., *Met. Ind. (N. Y.)*, 29, 529 (1931); Wernlund and Oplinger, U. S. Patent 1,919,000 (1933).

[25] Hothersall, A. W., Clarke, S. G., and Macnaughton, D. J., *J. Electrodepositors' Tech. Soc.*, 9, 101 (1934).

[26] Hothersall, A. W., and Bradshaw, W. N., *J. Electrodepositors' Tech. Soc.*, 12, 113 (1937).

[27] Schlötter, M., *Metallwirtschaft*, 14, 247 (1935); British Patent 443,429 (1936); Pine, P. R., U. S. Patent 1,987,749 (1935).

The alkaline stannate bath has been found in general to be more suitable for the production of coatings of low porosity. Its superior throwing power is of no particular advantage in plating strip stock. While acid baths are less satisfactory from the standpoint of continuity of coating, they have the advantage of higher cathode efficiency and metal yield and low bath voltage; moreover, acid baths are operated at ordinary temperatures. It seems probable that it will be possible to electroplate steel strip in the acid bath at speeds comparable to those of the hot-tinning process.[7]

Tin Coatings by the Immersion Process

Tin may be deposited from solution in the form of a very adherent, although very thin, coating without the application of an external electromotive force such as is necessary in ordinary electroplating. The fundamental principle is, of course, the same in both. In this case, however, the necessary current arises from the contact of the dissimilar metals immersed in the solution. The process has found application for small articles of brass, iron or steel such as safety pins, thimbles, buckles, and many other objects for which a bright finish is desired.[28]

In one process the brass articles, after being cleaned, are piled on wire trays, with thin perforated sheets of tin "sandwiched" in at intervals, and are immersed for 3 or 4 hours in a hot (90° C., 194° F.) solution of sodium chloride and potassium acid tartrate (cream of tartar, $KHC_4H_4O_6$). The tin which forms the anode of the couple, passes slowly into solution and is deposited upon the brass articles (cathode). Immersion in a solution of stannous chloride and sodium hydroxide at the same temperature has also been found to be a satisfactory method for coating brass.

In a slightly different process, scraps of zinc are mixed in with the brass articles which are immersed in a solution of stannous chloride and cream of tartar. The zinc is the anode in this case, and as it passes into solution tin is deposited from the solution upon the brass (cathode). The electrolyte, of course, is gradually depleted of its tin. This process is usually carried out in a rotating barrel, and a period of 2 to 4 hours at 80° C. (175° F.) is required.

For tinning iron or steel a slight modification of the method has been found necessary. The solution contains ammonium alum in addition to the substances named above. The solution is kept hot and a period of about 45 minutes is usually sufficient. In all cases the articles are thoroughly cleaned by rinsing with hot water after the plating solution has been drawn off, after which they are dried and polished somewhat by sawdust, bran, or macerated leather. Although the coatings as deposited are very much brighter than those made by electroplating, coatings made by this method are extremely thin but very uniform. It is not possible to form a heavy coating by this method since the deposition of tin necessarily ceases as soon as the surface is covered. Although the method is an old one and is of some commercial importance, it is still carried on in a strictly empirical manner.

---

[28] Proctor, C. H., *Met. Ind. (N. Y.)*, **12**, 64 (1914).

TINNING OF COPPER

Copper is tinned on a commercial basis both by hot-dipping and by electroplating. A good deal of copper roofing is tinned, usually on one side only, and is generally done by hand. In tinning copper sheet by hand, the cleaned sheet is heated from beneath by some suitable means, and a small amount of flux (ammonium chloride or a solution of zinc chloride) and a few strips of pure tin are dropped on the heated surface. By rubbing with a wad of cotton waste a relatively uniform coating is obtained.[29]

The hot-tinning of copper articles is carried out in much the same manner as the hand-dipping of steel parts. The flux employed is generally an aqueous solution of zinc and ammonium chlorides. The period of immersion in the tin bath is only long enough to bring the article to the temperature of the tin bath and permit free draining of the tin upon removal. The coating so produced invariably contains a small percentage of alloyed copper.[30] At the copper-tin interface a duplex layer consisting of the compounds Cu_3Sn and Cu_6Sn_5 is formed, but this layer breaks up under solvent attack, leading to contamination with copper of both the tin bath and the tin coating. There is evidence that in tinning ordinary copper containing cuprous oxide inclusions a small proportion of copper in the tin bath (about 1 per cent) is conducive to smooth coatings.[30] Cuprous oxide inclusions do, however, contribute to porosity of the tin coatings.[31] Such inclusions are readily removed from the copper surface by cathodic treatment in dilute caustic soda solution.

The tinned copper pipe used in refrigeration equipment is usually produced by hot-dipping.[32] Of late, however, electroplating has come to play a large part in the production of tin-coated copper and brass coils and other parts for refrigerators. Some of this is plated by semi-automatic methods.[33] Both acid sulfate and alkaline stannate baths are used in this work, although the latter seems to be preferred because of its greater throwing power—an advantage in plating parts of irregular shape.

The tinning of copper wire which is to be covered with rubber insulation is a very common practice. The tin layer guards against the corrosive attack on copper by the sulfur in the rubber, and likewise deterioration of the rubber by contact with the copper is prevented to a large extent. Where long life and a continued high degree of adhesion of the rubber are required, tin coatings are, however, inadequate. Pinholes in the tin coating permit the gradual ingress of sulfur vapor and a corrosive attack on the copper follows; this results in loosening of the insulation and acceleration of its aging.

---

[29] Krom, L. J., *Met. Ind. (N. Y.)*, 11, 122 (1913); Monroe, H. F., *Metal Worker*, 474, 83 (1915).

[30] Daniels, E. J., *J. Inst. Metals*, 58, 199 (1936).

[31] Jones, W. D., *J. Inst. Metals*, 58, 193, (1936).

[32] Daniels, E. J., and Macnaughton, D. J., *Proc. British Assn. of Refrigeration*, 33, [1] 78 (1936-37).

[33] Shields, A. L., *Monthly Rev., (Am. Electroplaters' Soc.)*, 22, No. 7, p. 15 (1935).

THE USE OF TIN-PLATE IN THE CANNING INDUSTRY

The United States is the largest producer of canned goods in the world. In 1935 these included 164 million cases of canned vegetables and soups, 40 million cases of canned fruits, and 12 million cases of canned fish. Besides these products something like 2 billion pounds of milk and 150 million pounds of meat are canned annually; and even dog food was represented to the extent of 476 thousand cases! In the second year that cans were used for beer about 600 million cans were required. All told, it is estimated that 17 billion containers were made from tin-plate in 1937.

The process of preserving foodstuffs by means of heat was discovered in the late 18th century by Nicholas Appert, who was awarded a prize offered by the French government for a successful method of preserving food for the army.[34] The first mention of the tin-plate container was in a patent granted in England in 1810 to Peter Durand. A few years later William Underwood introduced the canning of fruits and vegetables into New England, but it was not until the time of the Civil War that the industry became well established in America.

The development of the tin can from the crude cannister of Durand down to the latest improvement, the beer can which is capable of withstanding internal pressures, is the work of numerous inventors. When cans were made by hand, the output of an industrious workman under favorable conditions was a hundred a day. At the present time a hundred cans are made with a sequence of machines in a can-making line in twenty seconds.

The tin-plate from which most cans are made is of the coke quality, that is, the thickness of the tin is from 0.00006 to 0.00015 inch. This corresponds approximately to 1 to 2.5 pounds of tin per base box or from 1.0 to 2.5 milligrams per square centimeter of surface.

The fabrication of the simple type of can is accomplished as follows.[35] The bodies (sides) and ends (tops and bottoms) of the cans are cut from sheets of tin-plate, the side seam crimped and then fluxed and soldered from the outside. The two rims of the cylindrical body are curled outward in order that the ends may be sealed on. The bottom is put on by the can manufacturer and the top by the canner, but both by the same method. The rims of the end parts are curled to fit over the ends of the body and a thin film of rubber compound applied in this curl. The sealing operation

[34] Macnaughton, D. J., and Hedges, E. S., *Internat. Tin Res. and Dev. Council,* Bull. No. 1, February, 1935.

[35] "The Story of the Tin Can," National Canners Assn., Washington, D. C.

consists in making a tight double-crimped seam which is made air-tight without the use of solder.

In cans which are enameled on the inside, the enamel is applied to the tinned sheets before fabrication of the can. Two general classes of enamels are used, one to prevent blackening of the cans by the sulfur compounds present in meats and certain vegetables, and the other to prevent the bleaching of certain highly colored fruits. Beer cans are given two coats of enamel and baked twice.[36]

Canned food products range in acidity from about pH 2.6 to pH 6.8. Certain vegetables, notably the legumes and marine products[37] contain sulfur-bearing substances which may react with tin, producing a dark sulfide tarnish, as stated above, and this in turn discolors the contents of the can. Canned cream after some months' storage sometimes induces a "purpling" of the can, which has been shown to be due to a film of tin sulfide.[38]

One of the principal problems of the canned food industry is corrosion of the can. This may take the form either of perforation of the can or of swelling or bulging of the can due to an accumulation of hydrogen liberated by corrosive action. Recent studies indicate that silicon and copper in the steel base in excessive amounts may cause poor resistance to perforation in fruit packs.

CORROSION RESISTANCE OF TIN COATINGS

Performance in the Atmosphere

Upon exposure to the air tin becomes coated within a few hours with an invisible film of stannic oxide which greatly retards but does not prevent continuation of attack. Weight increment studies of specimens exposed indoors show that after the first three or four days the gain in weight with time is a linear function. This suggests that after the initial period the surface film is of a granular nature and not of the continuous protective type. It will be recalled that an analogous behavior is shown by zinc, although the actual value of the weight increment after 220 days in a comparative test indoors at Birmingham (England) was but 0.8 milligram for tin as against 3.0 milligrams for zinc for surface areas of 1 square decimeter.[39] When the tin surface was freshly scraped before the test there was a gain in weight of 1.2 milligrams. Undoubtedly the prevailing character of the atmosphere has an influence on specimens exposed indoors. For instance, at the end of 215 days, specimens of tin sheet exposed in telephone central offices at the following locations had gained in weight in milligrams per square decimeter of area as follows: Asbury Park, N. J., (sea-

---

[36] "The Development of a New Container—The Beer Can," an address by W. E. Taylor, The American Can Company, before Food Technology Conference, Mass. Inst. Tech., Sept. 15, 1937.

[37] Dill, D. B., and Clark, P. B., *Ind. Eng. Chem.*, **18**, 560 (1926).

[38] Jackson, C. J., Howat, G. R., Hoar, T. P., *J. Dairy Research*, **7**, 284 (1936).

[39] Kenworthy, L., *Trans. Faraday Soc.*, **31**, 1331 (1935).

Table 14.—Atmospheric Corrosion of Tin.

Location	Original Weight	Change in Weight, Grams			Tensile Properties after 6 Yrs.		% Change in Tensile Properties		Remarks
		1 Yr.	3 Yrs.	6 Yrs.	Tensile Strength	Elongation (%)	Tensile Strength	Elongation (%)	
Pittsburgh	464.38	+0.33	+0.39	.....					Severely distorted; deposit of some tar and silt. White spotty film, gray near edges. (One specimen missing.)
No. 1	463.64	+0.32	+0.66	+1.45	3035	61.8	−12.0(*4.3*)*	−1.0(*17.6*)	
Altoona	469.01	+0.45	+1.27	+2.42	2940	61.5	−14.8(*3.2*)	−1.4(*19.7*)	Black heavy film with white pitted scale, tinge of red (foreign source) at edge.
No. 2	462.55	+0.46	+1.27	+2.57					
New York City	470.83	+0.50	+0.89	+1.48	3061	60.7	−11.3(*3.0*)	−2.7(*24.6*)	Dirty dark gray film, small amount white pitted scale.
No. 4	470.43	+0.52	+0.92	+1.49					
Rochester	464.92	+0.33	+0.53	+0.87	3145	59.1	−8.9(*2.2*)	−5.3(*14.7*)	Spotty whitish tarnish, few pits.
No. 6	466.23	+0.32	+0.55	+0.88					
Sandy Hook	470.64	+1.04	+1.24	+2.20	2945	41.1	−14.6(*3.4*)	−34.1(*15.2*)	Surface speckled with white scaly spots with pits beneath.
No. 5	472.62	+1.00	+1.19	+2.07					
Key West	465.64	+0.43	+1.12	+2.74	3002	57.3	−13.0(*2.3*)	−8.2(*17.5*)	White speckled film with scale at edges.
No. 7	467.58	+0.47	+1.17	+2.82					
La Jolla	470.68	+1.50	+2.40	+3.87	2788	20.8	−19.2(*4.1*)	−66.8(*26.3*)	Spotty white scale areas with pitting, yellowish spots in heaviest scale.
No. 9	468.04	+1.45	+2.16	+3.71					
State College	469.23	+0.19	+0.22	+0.25	3157	68.5	−8.5(*2.8*)	+10.1(*16.2*)	Light film with white pitted scale.
No. 3	471.13	+0.17	+0.21	+0.23					
Phoenix	467.84	+0.14	+0.19	+0.34	2997	59.2	−13.1(*1.8*)	−5.1(*21.2*)	White speckled film, slight pitting.
No. 8	470.34	+0.14	+0.20	+0.93					

* Italic figures in parentheses indicate maximum percentage difference due to chance.

side) 0.151; New York City (industrial) 0.114; and Rockaway, N. J. (rural) 0.089. These specimens had been carefully cleaned for the test by abrading under water with levigated alumina, washing in water and then alcohol and quickly drying.

The behavior of tin exposed directly to the outdoor air is influenced by rainfall, atmospheric pollution and particularly by chlorides which are prevalent in marine locations. In Table 14 are given the values after 1, 3 and 6 years for change in weight and change in tensile strength and percentage elongation of tin specimens exposed to the atmosphere in nine localities by Committee B-3 of the American Society for Testing Materials.[40] The area of the specimens employed in the gravimetric tests was 216 square inches, (13.9 dm^2). It will be recalled that Pittsburgh, Altoona and New York City are industrial in character, Rochester urban, Sandy Hook, Key West and La Jolla, marine, and State College and Phoenix rural, the latter being in an arid region. It should be mentioned that the test specimens at Pittsburgh were submerged under 10 feet of flood-water for several days during March, 1936, which date is between the third and sixth year period of exposure.

It will be observed that the three marine locations provided the most corrosive conditions; this is shown particularly by the loss in percentage elongation. Industrial atmospheres appear to be definitely more severe in attack on tin than do the less polluted country atmospheres. The outdoor air of Birmingham is even more corrosive than that of any of the American industrial localities given in Table 14, the weight increment obtained after one year of exposure being 66 milligrams per square decimeter, or 0.92 gram calculated to the areas employed in the A. S. T. M. test. The relative humidity of the atmosphere apparently has little accelerating effect upon the corrosion of tin until it attains a value of 85 per cent. This conclusion is based upon the results of an experiment on the deliquescence of corrosion products detached from a corroded specimen of tin.[39]

The corrosion of tin-plate exposed to the atmosphere is characterized mainly by rusting at pinholes in the coating. As is well known, iron is anodic to tin under conditions of exposure to the atmosphere and when immersed in water and many solutions. Unlike zinc, tin does not protect iron cathodically in these environments. Consequently the performance of tin-plate is determined largely by its porosity. All commercial tin-plate whether of the coke or charcoal variety is porous or discontinuous. Although it is claimed that coatings of the order of 100 grams per square meter (approximately 9 pounds per base box or 0.0005 inch in thickness) can be produced free from pinholes,[41] this is difficult to accomplish on a commercial scale. In an investigation of the relation of coating thickness to porosity, it has been reported that the number of pores per 100 square centimeters falls from 8000 to 300 as the thickness of coating is increased from 1 to 3 pounds per base box. Further improvement is obtained with greater difficulty since increasing the coating thickness to 15 pounds per base box reduced the number of pores from 300 to 2.[42]

---

[40] Finkeldey, W. H., *Proc. Am. Soc. Testing Materials*, 38, (1938).

[41] Peter, F., and Le Gal., G., *Archiv. Eisenhüttenwesen*, 9, 285 (1935).

Pores in tin-plate arise from a variety of causes. Among the factors which may be responsible are surface cleanness of steel sheet, pickling procedure and cleanness of the flux. It has been suggested that the occurrence of pinholes may be due to hydrogen absorbed in the pickling operation which is then liberated upon tinning.[43] Other investigators have disputed

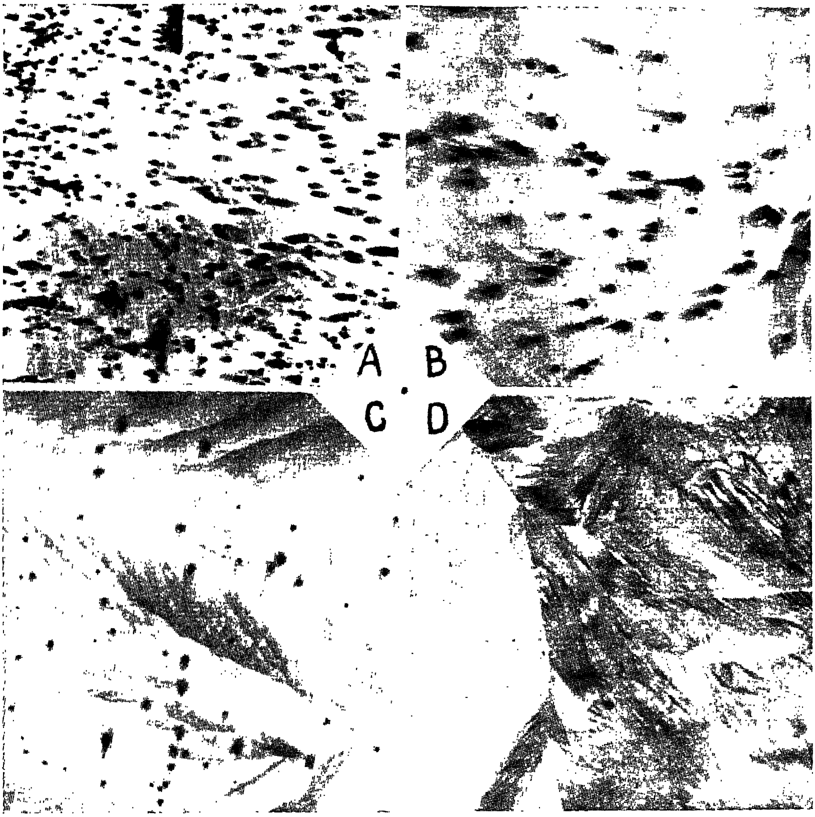


Figure 33.—Porosity of Composite Coatings of Hot-Dipped and Electrodeposited Tin (After Hot-Water Test).[45]

A. Blank Tin-Plate 1.5 lbs. per Base Box. 1150 Pores per sq. dm.
B. As (A) with 0.25 lb. Electrodeposited Tin per Base Box. 116 Pores per sq. dm.
C. As (A) with 1 lb. Electrodeposited Tin per Base Box. 76 Pores per sq. dm.
D. As (A) with 8 lb. Electrodeposited Tin per Base Box. No Pores.

---

[42] Hoare, W. E., *J. Iron and Steel Inst.*, **136**, 99 (1937).

[43] *Mitt. Materialprüfungsgamt und Kaiser Wilhelm Inst. Metallforschung*, new series No. 3, p. 58 (1926).

this explanation of the origin of pinholes[41] but it is generally conceded that evolution of hydrogen is a factor in blistered coatings. The occurrence of pinholes in electrodeposited coatings may be caused either by the character or cleanness of the steel surface, or by factors associated with the plating bath and its operation, such as, for example, suspended dirt particles, precipitation of basic salts, etc.

The porosity of tin-plate may be reduced by superimposing an electrodeposited layer of tin upon the hot-dipped product.[44] This has been done from an alkaline bath with the following results:[45]

Tin added by plating (lb./base box)	nil	0.25	1.0	2.0	4.0	8.0
Porosity (pores/sq. dm.)	1000	135	44	30	5	0

The behavior of the composite coatings on outdoor atmospheric exposure was in line with the porosity results. Their average porosity was found to be from 5 to 10 per cent of that of hot-dipped coatings of the same thickness. A comparison of the pores in these coatings revealed by testing them in hot water is shown in Figure 33.

The deformation of tin-coatings incident to the fabrication of articles from tin-plate may have a serious effect upon their protective value. A microscopic study indicates that forming and drawing operations cause surface fractures in the steel base which in turn cause discontinuities in the tin coating. A comparative study[46] made recently on hot-dipped and plated coatings has shown that the resistance to increase in porosity by deformation produced by stretching was strikingly different from the order of protective value of the various coatings in the unstretched condition. The average values of porosity obtained for the various unstretched tin coatings in this study are given in Table 15. The rough matte deposits from the acid bath were obtained from baths containing an inadequate percentage of addition agents, the smooth matte when the bath contained an intermediate amount of such agents, and the bright (actually semi-bright) from solutions containing a relatively high proportion of addition agents.

Table 15.—Porosity of Tin Coatings of Various Types of Tin Coatings.

Type of Coating	Pores for sq. dm. for coatings of thickness 0.00012 inch	Pores for sq. dm. for coatings of thickness 0.0003 inch
Hot-dipped (tin-plate)	616	156
"Alkaline" tin deposit	646	32
Composite (1:3 electrodeposited tin: hot-dipped tin)	98	5
Rough matte "acid" tin deposit	1034	200
Smooth matte "acid" tin deposit	530	42
Bright "acid" tin deposit	393	40

---

[44] Macnaughton, D. J., British Patent 417,411 (1933).

[45] Hothersall, A. W., and Bradshaw, W. N., *J. Soc. Chem. Ind.*, **54**, 320T (1935).

[46] Macnaughton, D. J., and Prytherch, J. C., *J. Electrodepositors' Tech. Soc.*, **12**, 66 (1937).

The superiority of the composite coating is again demonstrated in these results. It is evident also, as has been pointed out previously, that deposits from the alkaline plating bath are usually somewhat less porous than are those from acid solutions.

The porosity results obtained upon stretching the lighter-weight coatings listed in Table 15 are shown in Figure 34, in which the number of pores developed in the hot water test (described in Chapter 12) are plotted against per cent stretch on specimens 2 inches in length and 0.5 inch in width. The values for the heavier coatings (0.0003 inch) subjected to the same treatment were found to fall in the same order as the values for the lighter coatings here shown, although of course the range of porosity was much lower.

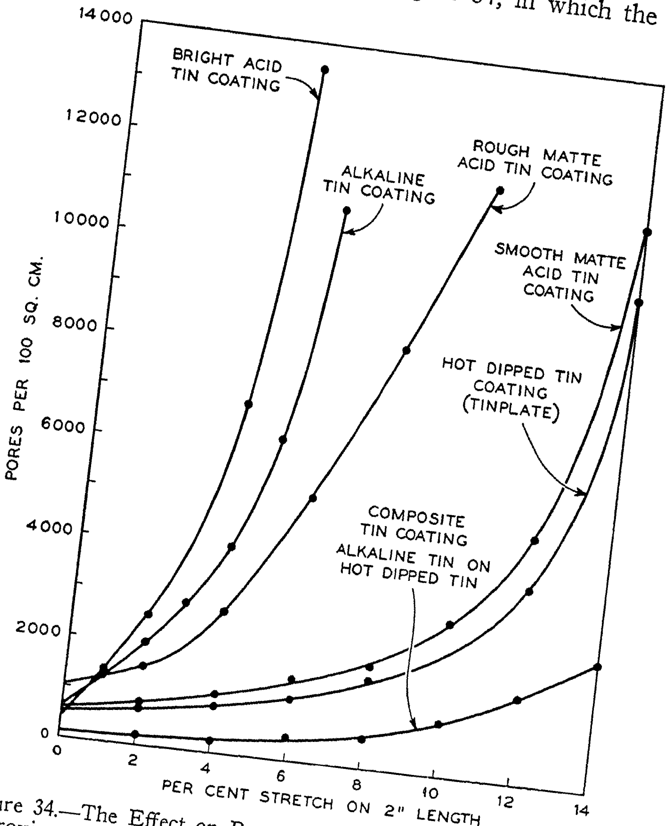


Figure 34.—The Effect on Porosity of Stretching Tin Coatings Approximately 0.00012 Inch Thick on Mild Steel, Approximately 0.1 Inch Thick.[46]

The performance of the composite coating is shown to be outstandingly good. From the standpoint of cost, however, it seems unlikely that such coatings can be used for such articles as tin cans. It is of interest to note that the smooth matte coating from the acid bath behaves most nearly like that produced by hot dipping.

The severe local porosity caused by bending tin-plate may be reduced by the subsequent electrodeposition of tin on the bent surface.[45] For example, it has been reported that the porosity of bent tin-plate of 1.25 lb. per base box quality on which 0.25 lb. (2.8 g. per sq. m.) of tin has been electrodeposited subsequent to bending is similar to that of a hot-dipped coating of 10.5 lb. per base box quality. It has long been common practice in the manufacture of the better grade of articles from tin-plate, such as kitchen utensils, to retin them after fabrication, but this has usually been done by means of hot-dipping; presumably this might well be accomplished by electroplating.

A distinction is usually made between normal pores, which are cavities extending through the tin coating to the steel base, and what is known as potential pores, which are defects in only the outer tin layer of the coating. Careful optical studies made on a specimen of tin-plate with a coating thickness of 0.00018 inch showed that in a particular instance the diameter of the affected area of the coating in the case of normal pores was 0.0125 inch, while the diameter of the steel base exposed was 0.002 inch.[47]

Potential pores at low magnifications appear to be areas of increased roughness. The term includes grease lines, which are regions in which much of the tin has been stripped by runnels of oil formed in the nip of the top pair of grease-pot rolls; it also includes mottle or "dry patches" which are areas of exposed $FeSn_2$ crystallites produced in some obscure manner.[48]

The degree of protection against corrosion afforded by potential pores is considerable unless the coating is subjected to mechanical operations such as drawing, forming, bending, etc. Under these circumstances the $FeSn_2$ layer, owing to its brittle nature, breaks down and exposes the underlying steel base.

If the mottled area is extensive it may cause a sheet of tin-plate on which it appears to be rejected as a "mender." In the inspection of the finished plates, which is a "100-per cent" inspection, the sheets are classed as (a) primes, (b) seconds, (c) menders, and (d) waste. The "prime" sheet is not a perfect sheet, but in general is as good as can be made by present means for the particular grade of plate under consideration. The "menders" are sheets which by being retreated, usually by redipping in the molten tin, after a little cleaning, can be improved and put into class (a) or (b); the "waste" is, as the name implies, more or less of a loss although, in the form of strips and other small pieces, much of it is salable. The "seconds" were formerly known as "wasters," a term often not clearly understood by the purchaser. A "second" is a sheet which because of certain defects, usually of limited extent, requires that extra care be taken in its usage. For can making, for example, if a second has only a ragged edge it is for all practical purposes as good as a prime sheet. If it contains a number of bare spots, the part remaining after discarding the bare areas is essentially the same as the first-class sheet. For some uses, however, which require an entire sheet, second sheets can not be considered at all.

---

[47] Hoare, W. E., and Chalmers, B., *J. Iron and Steel Inst.*, 132, No. 2 (1935).

[48] Hoare, W. E., *Proc. of Swansea Tech. College Met. Soc.*, Reprinted by Internat. Tin Res. and Dev. Council, *Series A*, No. 14 (1934).

The surface of hot-tinned sheets sometimes has an undulating or wave-like contour in the direction of tinning. These "ripple" marks have been found to consist of parallel ridges and valleys in the tin coating (at right angles to the direction of tinning). In one specimen, examined by means of an optical method involving the formation of interference fringes between an optical flat and the tin surface, it was found that the half-depth of the valleys was approximately one-third of the mean coating thickness.[47] There is also a somewhat similar effect of ridges and valleys in the coating lying *along* the direction of tinning.

"Yellow stain" is the name given to a golden yellow coloration which occasionally develops on the surfaces of tinned sheets after 3 or 4 months of storage. The stain may appear in patches or over most of the area of the sheet, except the edges which are usually free from it. It is a film strongly adherent to the tinned surface and cannot be removed by heat, organic solvents or dilute acids or alkalies. Apart from the unsightly appearance of yellow stain it renders sheets unsuitable for lithographing purposes since the stained portions are not wettable by ink. As far as is known, yellow stain does not reduce the resistance of tin-plate to corrosion in the atmosphere and most solutions.

A recent investigation [49] has elucidated the mechanism of the formation of yellow stain and suggested a practical method of its removal from sheets. The resemblance of the stain to the oxidation tint on tin suggested that the stained areas were in reality regions of superficial oxide; and it was found experimentally that it was possible to produce by differential aeration in an electrolytic cell a yellow oxide film identical in appearance with the natural stain on commercial tin-plate. The film appeared on the anode of the cell, while the cathode around which oxygen was bubbled remained in its highly polished condition. Furthermore, it was found that both the experimentally formed film and the natural yellow stain could be removed readily by cathodic reduction—a result which indicated the practical usefulness of this method for the treatment of affected commercial sheet. In view of these results it is reasonable to assume that yellow stain is produced by differential oxidation arising from conditions which affect the uniformity of exposure of the surface of the sheet to the air. Factors such as the distribution of oil or grease over the sheet or uneven contact with sheets or objects may well, under conditions of moderately high humidity, induce such differential oxidation.

---

[49] Beynon, C. E., Leadbeater, C. J., and Edwards, C. A., *Tech. Pub. Internat, Tin, Res. and Dev. Council, Series D,* No. 1 (1935).

Performance in Aqueous Solutions

It may be inferred that the relationships between defects characteristic of tin coatings (such as porosity) and corrosion resistance, which have been discussed in the previous section dealing with atmospheric exposures, are valid for tin-plate submerged in water and aqueous solutions. It is true that in the majority of solutions the exposed areas of iron rust, a notable exception being in solution of certain organic acids in which, as will be described later, tin corrodes in preference to iron. Inside of tin cans and in the absence of air continuity of coating is less essential than it is in outdoor exposures.

Pinhole corrosion of tin-plate has always been a disadvantage in its use for certain kitchen ware and utensils, with the result that years ago vitreous enamel coatings, glassware and aluminum had little difficulty in invading the field. However, tin-plate still finds wide use because of its cheapness. The use of tin-plate for baking dishes presents no difficulty since the pores become plugged with grease.

The resistance of block tin to water is responsible for its use in pipes and equipment for handling distilled water. Carbonated water, also, has practically no solvent action on tin. This is in considerable contrast to lead which is readily corroded in distilled water. Even in sea-water tin is corroded markedly less than are the other common non-ferrous metals.[50] Tin-plate, on the other hand, usually develops pinhole corrosion, particularly in saline solutions if air is present. It is true that the air-formed film on tin-plate affords a measure of protection for short periods of exposure to water and neutral salt solutions.

In the use of tin-plate in nearly neutral solutions, such as water, dairy products and certain canned foods, corrosion of a localized type characterized by "black spots" occurs. These spots are black by diffuse light but may appear grey by oblique light. They are irregular in shape and usually extend along scratches in the plate. These spots may vary from microscopic sizes to areas of one or two square centimeters. It is easy to produce "black spots" experimentally by immersion of tin-plate in neutral salt solutions. The presence of copper as an impurity promotes development of the spots although it is not essential for their appearance, since similar behavior is exhibited by tin of high purity.

The mechanism of the formation of "black spots" has been studied by electromechanical methods.[51] It was found that before the development of the spot, the tin surface becomes more noble, owing to the repair of any defects in the air-formed film. The repairing process is one of anodic oxidation, since defects in the film become anodic areas upon immersion. When, however, the anodic area at the base of a pit becomes sufficiently polarized due to deficiency of anions, it is suggested that dissolution of stannous ions occurs, causing undermining and breakdown of the film. The point of breakdown then becomes a microscopic anode of sufficiently high anodic current density to produce a black spot of oxide. By chemical analysis the black corrosion product has been shown to consist of a mixture of stannous and stannic oxides, mainly the former.

---

[50] Friend, J. N., *J. Inst. Metals*, 39, 111 (1928).

[51] Brennert, S., *Tech. Pub. Internat. Tin Res. and Dev. Council, Series D*, No. 2 (1935); Hoar, T. P., *Trans. Faraday Soc.*, 33, 1152 (1937).

Tin is corroded rapidly in strong alkalies, the attack apparently increasing progressively with increase in alkalinity beyond about pH 8.5 [52] and in ordinary acids exposed to the air; it is rather resistant to attack by dilute acids in the absence of air, as is illustrated in Table 16.[53] The process of corrosion in the latter case is controlled by the rate of cathodic depolarization, and since the hydrogen overvoltage of tin is high, the rate of corrosion is low in the absence of depolarizing agents such as oxygen (or nitrate in the nitric acid solution). In higher concentrations of strong acids tin corrodes more readily owing to the development of corrosion cells of sufficient potential to discharge hydrogen at tin cathodes. The presence in tin of metallic impurities of lower hydrogen discharge potential should increase corrodibility, particularly in acids. The deleterious influence of copper which was observed [54] when copper-bearing tin specimens were immersed in dilute hydrochloric and citric acids exposed to air might be expected to persist in the absence of air.

Table 16.—Corrosion of Tin in Ordinary Acids.

		Mg. per sq. dm. per day	
Acid	Conc. %	Hydrogen	Oxygen
Nitric	3	630	640
Hydrochloric	6	60	11,100
Sulfuric	6	35	4,300
Acetic	6	15	2,300

The behavior of the tin-iron couple, as exemplified in tin-plate, has been the subject of considerable investigation. The matter is of particular importance in connection with the use of tin cans in the fruit canning industry. It would be expected from the acidity of these products, and the electrode potential relationship of tin and iron, that perforation of cans would be very common. While it is true that some of the more acid fruits, notably Bing cherries and certain berries, do give trouble, particularly if stored at relatively high temperatures,[55] perforation of cans is not a source of serious loss. It is clear, from general experience in the canning industry, that anodic dissolution of the exposed steel base at pores in the tin coating is either retarded or entirely prevented.

---

[52] Derge, G. J., *Am. Inst. Mining Met. Eng. Tech. Paper,* No. 913 (Feb., 1938).

[53] Whitman, W. G., and Russell, R. P., *Ind. Eng. Chem.,* **17,** 348 (1925).

[54] Hoar, T. P., *J. Inst. Met.,* **55,** 135 (1934).

[55] Kohman, E. F., *Nat. Canners' Assoc. Bull. 22L,* p. 11 (1927).

Electromotive force measurements of the tin-iron couple some years ago disclosed an unsuspected variability of behavior.[56] First observed in several strong electrolytes and later in certain fruit juices and organic acids, this variability of e. m. f. was recognized as having a bearing upon the problem of tin can corrosion. The measurements showed that the iron in the tin-iron couple was initially anodic, a relationship to be expected, but within a few minutes a reversal of potential occurred in which the iron became cathodic and remained so. A later more exhaustive investigation of the phenomenon[57] employing current-time, potential-time, and loss of weight measurements has been illuminating. A summary of the results obtained for the direction and magnitude of current in the couple is given in Table 17. In every case (although not shown in the table), tin and iron gave initially high (noble) potentials which fell rapidly to low values. Evidently the first effect is the breakdown of the initial oxide film. The results compiled in Table 17 show that, following the film breakdown, iron is initially anodic in the presence of citrates but becomes cathodic in time, while the reverse behavior is shown for the couple in sulfuric acid. In oxalic acid, however, iron is the cathodic element throughout the experiment. Couple current studies in citric acid, made as a part of this investigation, showed that the current rose rapidly to a high value after the reversal of potential and then fell rapidly to a small constant value of a few microamperes which was appreciably less in the absence of air than under conditions of air saturation. The results of corrosion tests on tin and iron alone and coupled together made in dilute solutions of citrate ions at pH 2.0 and at pH 5.0 are given in Table 18. Experiments were conducted both in the presence and in the absence of air.

Table 17.—Direction and Magnitude of Current in Tin-Iron Couple in Dilute Acid Media

In 0.1*M* citric acid:	Iron initially anode, became cathode after 5-10 sec. Current after 5 mins.: c. 0.75 ma.
In 0.1*M* citrate buffer:	Iron initially anode, became cathode after 40-100 secs. Current after 5 mins.: c. 0.25 ma.
In 0.1*M* oxalic acid:	Iron cathode throughout. Current after 5 mins.: c. 1.0 ma.
In 0.01*M* sulfuric acid:	Iron initially cathode, became anode after c. 1 sec. Current after 5 mins.: c. 0.3 ma.

From the foregoing account it becomes possible to understand the behavior of tin-plate in the presence of dilute acids when exposed to the air and when used in sealed containers. The initial polarity of the couple

---

[56] Mantell, C. L., and King, W. G., *Trans. Am. Electrochem. Soc.*, 52, 435 (1927); Kohman, E. F., and Sanborn, N. H., *Ind. Eng. Chem.*, 20, 1373 (1928); Lueck, R. H., and Blair, H. T., *Trans. Am. Electrochem. Soc.*, 54, 257 (1928).

[57] Hoar, T. P., *Trans. Faraday Soc.*, 30, 472 (1934).

Table 18.—Corrosion of Tin and Iron Alone and in Couple.

Weight loss in 48 hours. Temperature 18-22° C.
Mean of Duplicates.

1		2	3	4	5	6	7	8	9	10	11	12
	Liquid Corroding	Quantity of Electricity Passed by Couple Coulombs	Sn Alone mg.	Sn with Fe in same Vessel mg.	Sn Coupled to Fe mg.	Increase of Sn Corrosion Caused by Coupling mg.	Weight of Sn++ Equivalent to Quantity of Electricity Passed mg.	Fe Alone mg.	Fe with Sn in same Vessel mg.	Fe Coupled to Sn mg.	Decrease of Fe Corrosion Caused by Coupling mg.	Weight of Fe++ Equivalent to Quantity of Electricity Passed mg.
Air-Saturated	0.1*M* citric acid pH 2.0	4.03	2.25	2.1	4.2	2.1	2.4	3.95	2.5	1.1	1.35	1.2
	0.1*M* citrate buffer pH 5.0	5.15	0.9	0.9	3.9	3.0	3.1	1.4	3.0	1.55	1.45	1.5
Air-Free	0.1*M* citric acid pH 2.0	2.88	0.2	0.2	1.95	1.75	1.75	4.95	2.9	0.55	2.35	0.85
	0.1*M* citrate buffer pH 5.0	1.19	0.3	0.3	1.0	0.7	0.7	3.7	2.15	0.3	1.85	0.35

depends upon the relative potentials of the two metals coated with air-formed films. In sulfuric acid the oxide-coated iron electrode is the more noble, while in citric acid the reverse is the case. Upon dissolution of the films the potentials of the electrodes fall to values characteristic of the bare metals in the given electrolytes. In the presence of citrates and oxalates (and certain other organic acid radicals) tin forms stable complex ions restricting thereby the concentration of stannous ions and in consequence rendering the tin electrode markedly electronegative and anodic to iron. On the other hand, in sulfuric acid no complexes are formed, and the two metals stand in the general relationship to each other shown by their standard electrode potentials.

It is evident that in the tin can, where relatively oxygen-free conditions prevail, the rate of corrosion will be controlled by the rate of hydrogen evolution at cathodic areas. The foregoing work and that of earlier investigators has shown that in cans containing fruit acids the cathodic element is iron. Owing to the low hydrogen overvoltage of this metal sufficient hydrogen may be discharged to cause what is known as a "springer" or a bulging of the can. Since, however, but a small percentage of the pack develop springers, it is evident that the tin-iron cell is largely in a state of polarization. This fact suggests that substances are present in the food products which inhibit the cathodic discharge of hydrogen on iron in a fashion analogous to that produced by the use of organic inhibitors in the pickling of steel. As a matter of fact, it has been observed [58] that gelatin inhibits corrosion in canned fruits of high acidity but is without effect at low acidities. It will be recalled that the isoelectric point of gelatin is at pH 4.7 and that for acidities greater than that (lower values of pH) it is positively charged and migrates cataphoretically to the cathode. It seems evident, therefore, that this behavior of gelatin as a cathode inhibitor is illustrative of the mechanism by means of which corrosion of cans in highly acid media is retarded.

Perforation of the can at pores in the coating is minimized under the conditions mentioned in the foregoing discussion for the reason that the exposed iron areas are afforded cathodic protection. The addition of citric acid to fruits of low acidity has been shown to reduce corrosion markedly,[59] and this appears to be due to an increase in the efficiency of cathodic protection obtained in this manner. The greater tendency toward perforation reported for lacquered cans [60] may be due to the absence of cathodic protection at pores in the tin coating not covered with lacquer.

There is always a certain amount of corrosion of both tin and iron induced by local cell action on each metal. This accounts for the fact that salts of both tin and iron are found in the food products. Although there has been some controversy as to the toxicity of tin present in canned food, the consensus of opinion is that the quantities likely to be consumed are not harmful.

---

[58] Morris, T. N., and Bryan, J. M., *Dept. Science and Ind. Res. Food Invest.*, Spec. Report 40 (1931).

[59] Kohman, E. F., and Sanborn, N. H., *Ind. Eng. Chem.*, 25, 920 (1933).

[60] Kohman, E. F., *Food Manuf.*, 4, 292 (1929).

RECOVERY OF TIN FROM TIN-PLATE SCRAP

On account of the high price of tin and the very low price of tin-plate scrap, the recovery of the tin from such scrap has long been a subject of study and investigation. A great number of patents have been granted but only a few of the suggested methods have proved successful in practice on a commercial scale.

The early methods, which were based upon the use of such solvents as ferric chloride and stannic chloride, were too expensive and hence unsuccessful commercially. Likewise the "dry" metallurgical method of partially melting off the tin, together with oxidizing some of it to the form of "tin ashes" from which the tin was later reduced, was not a success. The two commercial methods used with considerable success today are (a) electrolysis in an alkaline solution and (b) treatment with dry chlorine.

In the electrolytic method, the tin-plate scrap, after being cleaned, usually with a hot solution of sodium carbonate, is compressed into bales of suitable size for handling. It is then made the anode of an electrolytic cell of which the other electrode may be a copper grid or the iron container for the solution. The electrolyte is a solution of sodium hydroxide containing some oxidizing reagent and is kept at approximately 70° C.)160° F.).

Tin is dissolved at the anode to form sodium stannite, from which tin is recovered at the cathode in a finely divided condition as a spongy deposit which after removal may be compressed, dried and melted. Experience has shown that a considerable excess of sodium hydroxide as well as of oxidizing reagent over the theoretical amount must be used. The bales of scrap, freed from the tin, are melted and used in the preparation of such products as sash weights. The use for steel making of scrap of this nature which may sometimes contain appreciable amounts of tin is not favored in American steel practice.

The tin may also be recovered from tin-plate scrap by means of an oxidizing alkaline solvent, such as sodium hydroxide and sodium nitrate, without electrolysis. By keeping the solution at the boiling point for several hours sodium stannate crystallizes from the solution, and can be separated from the liquid by a centrifuge. The stannate is usually converted to the form of tin oxide and is used in this form, principally in the enameling industry.

The chlorine treatment depends on the fact that *dry* chlorine at low temperatures readily reacts with tin but not with iron. The anhydrous stannic chloride which is formed drips off the clean baled scrap and is recovered and used as such. No attempt is made to obtain the tin from this, as the tetrachloride finds a ready market, particularly in the silk industry. Although the difficulties attendant upon this process are very great, the process has been developed so that now it is decidedly a commercial success.[61]

---

[61] Anon., *Met. Chem. Eng.*, 17, 187 (1917); Mason, M., *Met. Ind. (London)*, 23, 338 (1923).

Chapter 9

Nickel and Chromium Coatings

NICKEL COATINGS

Nickel has been used for many years as a protective and decorative coating for brass, iron and steel. It is applied to fabricated articles or parts, and recently, to sheets and wire. The method of application is largely by electroplating, although nickel-clad sheet produced by hot-rolling layers of nickel and steel in intimate contact is coming into commercial use. Nickel coatings may be obtained by spraying and this method of application, as well as electroplating, is finding increasing use in building-up worn surfaces. Nickel may be applied also by evaporation and sputtering methods, although nickel coatings so formed have not attained commercial importance.

Nickel possesses a combination of physical and chemical properties which make it widely useful as a coating metal. In strength, hardness and ductility it approaches mild steel, and nickel-clad steel is readily welded and hot-worked. Nickel is a relatively noble metal which maintains a more or less permanent white appearance in the air and possesses a high degree of resistance to corrosion by natural waters, sea-water, and neutral and alkaline salt solutions. Since nickel is not appreciably attacked by fruit acids, vegetable brines, dairy and meat products, and since its salts are considered to be non-toxic,[1] nickel and nickel-coated equipment is extensively used in the food industries.[2] The principal limitation of nickel as a coating metal lies in its electropositive relationship toward iron in most environments, a fact which makes necessary the use of relatively pore-free coatings for satisfactory protection of the basis metal.

With the development and widespread use of chromium plating in the past decade, nickel has assumed increased importance in its extensive use as an undercoating for this metal. Chromium coatings alone, in the thickness which is comparatively feasible, do not provide adequate protection to ferrous metals and consequently it is common practice to employ a protective undercoating which is usually nickel or a composite layer consisting of copper and nickel. It is customary to buff this undercoat in order to obtain the desirable bright appearance in the superimposed chromium finish. This chromium surface maintains its bright appearance almost unchanged by weathering. The development of "bright" nickel plating has provided an undercoating in which the buffing operation is unnecessary.

"Bright" nickel is an achievement of major importance in the metal coating field. While methods of obtaining lustrous deposits have been known for some time, it is comparatively recently that processes have been available for the rapid production of bright ductile nickel coatings of any desired thickness. This development has been greatly facilitated by the broader scientific knowledge of electroplating which has been obtained during the past few years.[3]

---

[1] Fairhall, Ray and Drinker, *J. Ind. Hygiene*, 6, 307 (1924).

[2] Tay, G. H., *Food Ind.*, 8, 60 (1936).

Heavy coatings of electrodeposited nickel have important uses outside the appearance and corrosion protection fields. In addition to such applications as the reproduction of printing plates, phonograph record plates, and the electroforming of tubes, sheets and other articles, heavy electrodeposits of nickel are increasingly employed in the engineering field in building up and surfacing worn and mismachined parts of all kinds.

Nickel Plating Solutions

The first record of nickel plating was in 1843. As an industry, nickel plating dates from 1870, following the invention in the previous year of the nickel-ammonium sulfate plating solution by Isaac Adams. This "double salt" solution remained in general use until about 1910 when it was gradually displaced for some uses by "single salts," *i.e.*, nickel sulfate.[4] In 1916 a nickel plating bath was proposed by Watts [5] which is typical of the "rapid" nickel solutions used since that time. This bath has a higher metal content, provided in the form of the sulfate and chloride, contains boric acid, and is operated "hot," *i.e.*, at 50-60° C., and at current densities from about 15 to 45 amperes per square foot.

At the present time a large number of bath formulas are employed in nickel plating. These are generally neutral or slightly acid solutions in which the nickel is present principally as the sulfate but which contain sufficient chloride to insure adequate anode dissolution. Boric acid is usually employed to regulate and control acidity and thereby to prevent precipitation of basic compounds at the cathode. Typical of solutions which have been widely used for plating nickel is the following:[6]

	Approximate Normality	Grams/liter	Oz./gal.
Nickel sulfate ($NiSO_4 \cdot 7H_2O$)	1.40	200	27
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	0.40	45	6
Boric acid	0.5 M	30	4

pH=5.3. Temperature 50-60° C. (122-140° F.)
Current density 1.5-5. amp./dm^2 (14-47 amp./sq. ft.)

More recently the trend has been toward the use of higher metallic ion concentrations,[7] higher current densities and higher acidities.[8] In the hot bath it is now common to employ 30 to 35 oz. per gallon of nickel sulfate (with the nickel chloride content given above), current densities as high as 80 amperes per sq. ft., and acidities of the pH range 1.5 to 3.5. Cathodic efficiencies are usually somewhat lower at the higher acidities. Relatively soft deposits are obtained in baths of the above type operated under these conditions. For harder deposits it is customary to employ lower metal concentrations, lower temperatures, current densities and acidities (pH 5.2 to 5.8). Sodium, potassium, ammonium or magnesium sulfates are often added to the plating solution to improve conductivity and throwing power. The sodium salt is said to be the most effective in this respect over a considerable range of acidity.[9] Throwing power is in general better in solutions of high pH than in those of low pH, and is improved by increasing the temperature.[10]

---

[3] McKay, R. J., *Metals and Alloys,* 7, 193 (1936).

[4] Hogaboom, G. B., *Inco (International Nickel Co.),* 13, No. 4, 12 (1936).

[5] Watts, O. P., *Trans. Am. Electrochem. Soc.,* 29, 395 (1916).

[6] Blum, W., and Hogaboom, G. B., "Principles of Electroplating and Electroforming," 2nd ed., New York, McGraw-Hill Book Co., 1930.

[7] Cotton, D. A., *Monthly Rev. Am. Electroplaters' Soc.,* 22, 6, (Dec., 1935).

[8] Phillips, W. M., *Trans. Am. Electrochem. Soc.,* 58, 387 (1930); Griffiths, W. T., (Paper before Electroplaters' and Depositors' Tech. Soc.). *Mond Nickel Co. Bull. L-4.*

Of the metallic impurities which may be found in nickel baths, iron is least objectionable even when present in relatively large amounts; in solutions of moderate acidity it is deposited as a solid solution with nickel. Iron may be oxidized to the ferric condition; and in baths operated in the customary low acidity range ferric iron will be precipitated as ferric hydroxide or basic ferric salts—products which should be filtered out to prevent their inclusion in the nickel deposit. Copper, if present in small amounts, will produce dark spots in nickel coatings. As little as 0.05 per cent zinc may give rise to streaky deposits.[6] Traces of lead may enter nickel plating solutions, being derived from lead-linings, heating coils or from the anodes. It is deposited with the nickel, yielding deposits of reduced grain size which are brittle and have a tendency to peel.[11] Aluminum, while not ordinarily an impurity in nickel salts, tends, if present, to accumulate in the cathode film forming colloidal compounds which give rise to burnt or black deposits.[12] It has long been known that organic contaminants in nickel baths are conducive to brittle deposits. Studies have lately shown that contact of nickel solutions with such materials as wood, cotton and silk may produce hard, brittle deposits usually lustrous in appearance.[13]

Nickel anodes tend to become passive, particularly in sulfate baths. Formerly cast nickel anodes containing several per cent of iron and usually other impurities were commonly used because of their greater solubility. With the growing recognition of the dependence of quality of the electrodeposit upon purity of solution, the use of anodes of higher purity has become prevalent. These anodes consist of rolled or cast metal and may average as high as 99.5 to 99.9 per cent nickel.[14] The uniformity of corrosion of rolled anodes may be improved by suitable annealing.[6] Nickel particles or inclusions produced in the dissolution of the anodes are prevented from reaching the bath by enclosing the anodes in bags made of cotton, glass or wool.

---

[9] Harr, R., *Trans. Electrochem. Soc.*, **68**, 425 (1935).

[10] Harr, R., *Trans. Electrochem. Soc.*, **64**, 249 (1933).

[11] Raub, E., and Wittum, M., *Korr. Metallschutz*, **13**, 261 (1937).

[12] O'Sullivan, J. B., *Trans. Faraday Soc.*, **26**, 533 (1930).

[13] Hothersall, A. W., and Gardam, G. E., *Met. Ind. (London)*, **50**, 609 (1937).

[14] Werner, E., *Metallbörse*, **24**, 1466 (1934).

Application of Nickel Plating to Aluminum and Zinc Alloys

Aluminum and its alloys, particularly die-casting alloys, are often plated with nickel, and this is usually followed with a chromium finish. In preparation for nickel plating it is essential that the aluminum or aluminum alloy surface be thoroughly cleaned and that it be roughened somewhat to insure adherence. A suitable surface condition may be obtained by mild sandblasting and by various etching reagents. Of the latter, a solution of nickel chloride (about $2N$) in normal hydrochloric acid or an acidified solution of ferric chloride [15] may be used for aluminum; for die-cast and sand-cast aluminum alloys a strong acid dip composed of 3 parts by volume of concentrated nitric acid and 1 part of 50-per cent hydrofluoric acid is desirable.[16] Another method of surface preparation for aluminum consists in immersion in dilute hot caustic (pH 10) containing chromates or silicates as inhibitors.[17] Another solution which has been proposed [18] as a preliminary dip is sodium zincate, which upon immersion deposits a superficial film of zinc on the aluminum surface. It is then plated by methods to be described presently for the nickel plating of zinc alloys. Nickel baths high in sulfate or containing citrates are generally employed in plating aluminum.

With the wide use of zinc-base die-castings in the automobile industry in recent years, nickel plating of these alloys has become general. Here again, the chromium finish is used for appearance. Door handles and radiator grills are conspicuous examples of nickel-chromium plated die-castings.

Zinc alloys of this type are polished either over the entire surface or only on the parting lines, usually buffed and then generally degreased with trichlorethylene in a three-stage system involving hot dipping, cold rinsing and a final vapor rinse.[19] All platers use an alkaline cleaner, commonly at 180° F., and in the majority of cases the castings are cathodically treated in such solutions. An acid dip consisting of 5- to 10-per cent hydrochloric acid or 5-per cent sulfuric acid is used to remove alkaline salts or superficial oxide, the work being left in the solution until there is evidence of gas evolution.

Zinc-base die-castings are plated either directly with nickel or with a composite copper-nickel coating. For relatively mild indoor use coatings of 0.0003 inch of nickel are common, while for more severe exposures, particularly for outdoor service, coatings 0.0008 to 0.001 inch in thickness (of which 0.0002 to 0.0003 inch is copper) are used. The solution for plating nickel directly is a low nickel-high sodium sulfate solution containing ammonium chloride and buffered in the pH range 4.9 to 5.7 by boric acid. In such a solution the ionization of nickel is repressed to such an extent that the deposition potential of nickel becomes electronegative to that of the alloy. Sodium citrate has been used in place of sodium sulfate to accomplish the same result by the formation of a complex ion which yields a low nickel-ion concentration.

---

[15] Ballay, M., *Trans. Electrochem. Soc.*, **62**, 91 (1932).

[16] Work, H. K., *Trans. Am. Electrochem. Soc.*, **53**, 361 (1928).

[17] Altmannsberger, K., *Chem. Ztg.*, **55**, 709 (1931).

[18] Fröhlich, W., *Metallbörse*, **24**, 405, 439, 469 (1934).

[19] Anderson, E. A. (N. J. Zinc Co.), *Private Communication*, June 11, 1938. Also, Metal Cleaning and Finish, **10**, 610, 614 (1938).

The copper solution used for depositing the copper undercoating in the copper-nickel finish is usually the Rochelle salt-alkaline cyanide bath described in Chapter 10. It is common practice to dip all copper-plated work in dilute sulfuric acid in order to neutralize traces of remaining alkali. Two separate nickel solutions may be employed for heavy nickel coatings. Most platers now use proprietary bright nickel solutions for the deposition of the final nickel coating; otherwise the Watts type bath is used and the deposit color-buffed for brightness.

Nickel coatings on aluminum and zinc-base die-castings have sometimes shown a tendency to peel off or blister under severe atmospheric corrosion if the coating is porous or abraded.

Applications of Heavy Electroplated Coatings

Nickel coatings, because of their superior wear-resisting properties, are used to a considerable extent on electrotypes and to a smaller extent on stereotype plates. They serve as protective coatings, not only in a mechanical sense by resisting wear, but also in a chemical way since they withstand the chemical action of colored ink much better than does copper.[20]

The use of heavy coatings of electroplated nickel on worn machine parts to provide fresh bearing surfaces and shafts which may be re-used [21] has been referred to previously. Similarly, heavy deposits of nickel are plated on articles which are subject to wear or erosion such as, for example, propellers, turbine blades, hydraulic rams, paper machine rolls, etc.

It has been shown [22] that by nickel plating brass articles which are subject to deterioration by season cracking resulting from the combined action of internal tensile stress and a surface corrosive attack, such deterioration can be prevented.

Bright Nickel Plating

The improvements made in the electrodeposition of nickel recently deserve special consideration. The importance of bright, smooth deposits as undercoatings for chromium has been mentioned. Equally promising and of widespread commercial use are bright deposits of sufficient softness to permit forming operations when the plating is applied beforehand to steel strip. Moreover, deposits of this kind may be obtained at current densities as high as 60 amperes per square foot.[3] The ductility of coatings of bright nickel applied by one of the new processes[23] is illustrated in Figure 35.

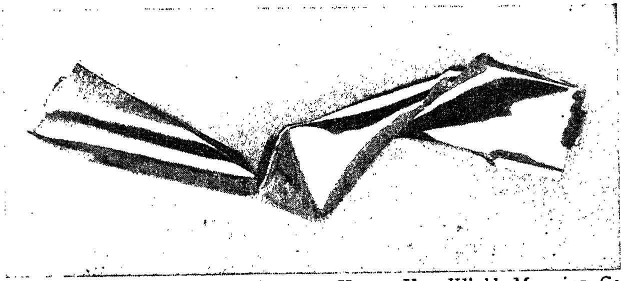
---

[20] U. S. Bur. Standards, Circular No. 100 (1924).

[21] Bonilla, C. F., *Trans. Electrochem. Soc.*, 71, 263 (1937).

[22] Moore, H., Beckinsale, S., and Mallinson, C. E., *J. Inst. Metals*, **25**, 35 (1921).

There are a number of processes for the production of bright nickel deposits.[24] As early as 1905 the use of ethyl nickel sulfate as a brightening agent was proposed in Germany. The presence in the plating bath of small proportions of zinc or cadmium was observed some years ago to produce bright deposits,[25] and colloids have long been known to give lustrous coatings. Glucose, malic acid, and gelatin have been shown to produce a marked improvement in the appearance of the deposits.[26]



Courtesy Hanson-Van Winkle-Munning Co.

Figure 35.—Steel Strip 0.016 Inch. "Bright" Plated with 0.001 In. Nickel. Deposit is Deformed to Illustrate Ductility.

The newer, patented bright nickel plating solutions usually contain nickel sulfate and chloride and boric acid, to which are added in small percentages a brightening agent which may be an aromatic polysulfonic acid derivative, an organic hydroxy-acid or its salt, a complex polyhydric alcohol, a zinc, cadmium or cobalt salt, or combinations of these. For example, one of these solutions[27] proposes the use of one gram per liter of benzyl naphthalene sodium sulfonate; another process[28] specifies 30 grams per liter either of nickel benzol disulfonate or naphthalene trisulfonate. Other processes employ less definite compounds as, for example, the reaction products of sulfuric acid with a terpenic compound,[29] an oleoresin,[30] or with petroleum.[31] Most of these baths employ wetting agents for the purpose of reducing the tendency to pit. Substances such as sodium gluconate, or sulfonated alcohols [32] may be used for this purpose. One of the most promising baths for bright nickel contains cobalt sulfate, nickel formate, and a small amount of formaldehyde.[23] In this process anodes containing 18 per cent cobalt are employed. The deposit obtained is a cobalt-nickel alloy similar in appearance and properties to bright nickel.

---

[23] Weisberg, L., and Stoddard, W. B. Jr., U. S. Patent 2,026,718, (Jan. 7, 1936).

[24] For resumé of patented processes of bright nickel plating, see Johnson, L. W., *Met. Ind. (London)*, 50, 281 (1937).

[25] Haring, H. E., *Trans. Am. Electrochem. Soc.*, 46, 107 (1924).

[26] Stout, L. E., *Monthly Rev. Am. Electroplaters' Soc.*, 23, May (1936), p. 25; Anon., *Metallwaren. Ind. Galv. Tech.*, 33, March 1, (1935).

[27] Lutz, G., and Westbrook, L. R., U. S. Patent 1,818,229, (Aug. 11, 1931).

[28] Schlötter, M., U. S. Patent 1,972,693, (Sept. 4, 1934).

[29] British Patent 436,042, (Nov. 3, 1934).

[30] Pine, P. R., U. S. Patent 2,029,386, (Feb. 4, 1936).

[31] British Patent 437,224, (Nov. 3, 1934).

The brilliance of nickel deposits from these baths is said to be due to fineness of grain size, which is of the order of the wave-length of light, and to the orientation of the crystals in the surface. Formerly, bright deposits were usually brittle and given to peeling. The present product, while harder than ordinary nickel deposits having the matte appearance, is reasonably ductile and is adherent if plated upon a suitably prepared base.

"Nickel-Clad" Steel

Nickel-clad sheet steel is made on a commercial scale.[33] The product is usually from $\frac{1}{4}$ to $\frac{1}{2}$ inch in thickness with a layer of nickel on one side comprising from 5 to 20 per cent of the weight of the entire sheet. This represents in the half-inch stock about 0.45 inch of steel and about 0.05 inch of nickel. The product is supplied in standard claddings of 5, 10, 15 and 20 per cent nickel. The nickel coating may be bonded to both surfaces of steel sheet. "Inconel," an alloy of approximately 78 to 80 per cent nickel, 12 to 14 per cent chromium and 6 to 8 per cent iron, may be employed instead of nickel as a cladding material.[34]

In making nickel-clad steel relatively heavy layers of steel and nickel are placed in intimate contact, heated to a temperature of about 2200° F. (1200° C.) and rolled to the finished plate. Inconel-clad steel is fabricated in an analogous manner. The bonding of the two metals in the case of the nickel-clad product is accomplished by superficial alloying at the steel-nickel interface. It is essential that the nickel surface be continuous, that all joints be strong and that all sheared edges be covered. Nickel-clad steel is finding useful applications in the chemical equipment field, particularly in processes dealing with brines, alkalies, acids, soaps, dyes, etc. Inconel-clad steel is suitable for equipment to be used in the brewing, distilling, textile, tanning and pharmaceutical industries.

Corrosion Resistance of Nickel Coatings

The protective value of nickel coatings is dependent largely upon their continuity. They function in most cases merely as physical barriers for the exclusion of air and moisture and do not at perforations in the coating afford electrochemical protection to exposed iron or steel. As in the case of tin-plate, pores in nickel coatings soon manifest themselves by the appearance of iron rust at those points.

---

[32] British Patent 438,412, (May 13, 1935).

[33] Humpton, W. G., Huston, F. P., and McKay, R. J., *Mining Met.*, 12, 90 (1931); Huston, F. P., *Internat. Nickel Co. Bull. T-4* (Sept. 1938).

[34] Theisinger, W. G., and Huston, F. P., "Metals Handbook," American Society for Metals, 1938.

Nickel exposed to air low in relative humidity and sulfurous gases remains bright in appearance for long periods of time. An invisible film of corrosion products forms under these circumstances as is proven by gains in weight of exposed test specimens. Figure 36,[35] illustrates with curves the weight increments with time of exposure of pure nickel specimens

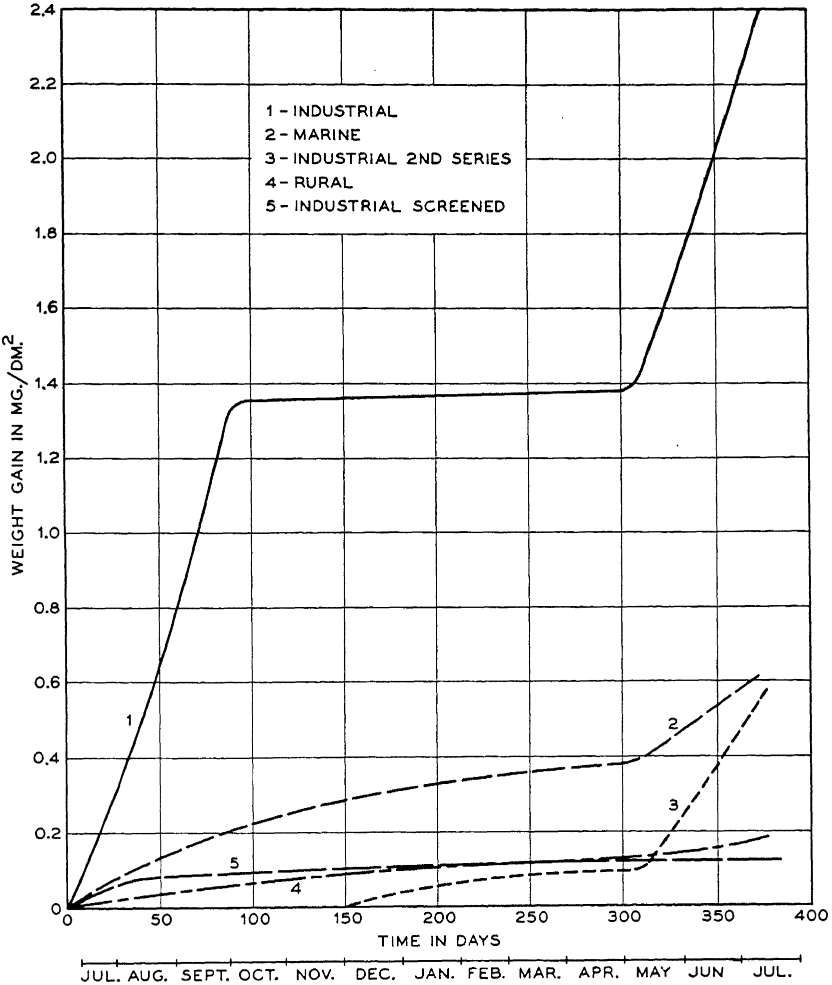


Figure 36.—Rate of Tarnish of Nickel in Various Indoor Atmospheres.

---

[35] Experiments by Messrs. W. E. Campbell and U. B. Thomas, Bell Telephone Laboratories, New York, N. Y.

placed indoors in heavy industrial (New York City), marine (Asbury Park, N. J.) and rural (Rockaway, N. J.) locations. It is seen that with the exception of the industrial station, the weight gains during the first 300 days were less than correspond to the thickness of visible films. It is of interest to observe in this figure that a similar result was obtained at the industrial location provided the nickel specimens were exposed in a "squirrel cage" surrounded by a muslin screen. The marked retardation of corrosion obtained by the use of muslin screens has been previously reported in studies on iron,[36] in which it was shown that rusting of specimens behind muslin was prevented, although a slight increase in weight occurred. The existence of an oxide film on nickel exposed to air of low relative humidity has been detected also by optical methods and it has been shown that this film is soluble in sulfuric acid.[37]

In air at relative humidities in excess of approximately 70 per cent[38] and containing sulfur dioxide in the quantities prevailing in industrial atmospheres (0.75-2.0 parts per million), nickel becomes covered with a cloudy film—a process known as "fogging." In the early stages the film may be readily wiped off, revealing the underlying metal surface to be still bright in appearance. Later, however, the fogging cannot be removed without abrading the metal. The weight-increment-time results obtained in the fogging of nickel are illustrated in Figure 36 by the curve for the specimens exposed at the industrial station. Fogging occurred only during the humid summer months since specimens set in December remained bright until May and then became cloudy in appearance. It should be pointed out that protective nickel coatings to be used in the atmosphere are now universally coated with a superficial layer of chromium which obviates fogging.

The mechanism of fogging apparently consists in the catalytic oxidation of sulfur dioxide to sulfur trioxide,[38] followed by corrosion of the nickel surface to nickel sulfate in the resulting film of sulfuric acid. That a catalytic process is involved is indicated by the fact that previous exposure of the fresh nickel surface to hydrogen sulfide markedly inhibits fogging—a reaction suggestive of the well-known poisoning effect of hydrogen sulfide on catalytically active surfaces. It is of interest to note that the rate of fogging is approximately halved when light is completely excluded. Chemical analysis of "fog" films formed in normal atmosphere has given the following results:[38]

After 21 days' exposure $NiSO_4 \cdot 0.26\ H_2SO_4$
After 88 days' exposure $NiSO_4 \cdot 0.33\ Ni(OH)_2$

Several tests have been made of the resistance of nickel to outdoor atmospheres. The results obtained by the Atmospheric Research Committee of the British Non-Ferrous Metals Research Association, after an exposure of one year in various atmospheres, are given in Table 19. The values reported are in terms of average thickness of corroded layer and are calculated from the experimental results for loss in weight of plate and wire specimens and for increase in electrical resistance of wire specimens.[39]

---

[36] Vernon, W. H. J., *Trans. Faraday Soc.*, 23, 159 (1927).
[37] Tronstad, L., *Z. physikal. Chem.*, 142, [A] 241 (1929).
[38] Vernon, W. H. J., *J. Inst. Metals*, 48, 121 (1932).

The greater severity of corrosion in the sulfur-bearing urban and industrial atmospheres is apparent. As in the case of zinc, marine atmospheres corrode nickel at a rate which is intermediate between that experienced in rural and industrial locations. The relatively greater intensity of attack shown for the electrical resistance method of test may be attributed to the greater circulation of air around wire specimens as compared with plate specimens, and also to the greater sensitivity of this method to penetration of attack along grain boundaries.

Table 19.—Average Thickness of Corroded Layer of Nickel Specimens Expressed in Millionths of an Inch Per Annum.

Exposure	Cardington (Rural)	Bournville (Suburban)	Wakefield (Industrial)	Birmingham (Urban)	Southport (Marine)
Stevenson Screen Wt. increment (wire)	64	97	227	245	141
Electrical Resistance (wire)	168	274	560	564	325
Weight-loss (plates)	45	96	218	230	111

Nickel is included in the comprehensive atmospheric corrosion test conducted by Committee B-3 of the American Society for Testing Materials, the results of which at the end of six years of exposure are given in Table 20.[40]

Here again nickel is seen to be corroded markedly more in the industrial atmospheres than at either rural or marine stations whether the deterioration is expressed as change of weight or loss in tensile strength. The urban air of Rochester, New York, and the sea air of the northern marine location, Sandy Hook, N. J. are of similar severity, while La Jolla, on the California coast, and Key West, Florida, are similar in mildness. Finally, it will be noted that the arid pure air of Phoenix, Arizona, is practically without action on nickel.

The foregoing discussion of the atmospheric corrodibility of nickel is applicable to nickel coatings of sufficient thickness to be practically pore-free and to provide thereby a continuous envelope of nickel about the base metal, iron, steel or brass, the protection of which is sought. Commercial nickel coatings are never entirely non-porous, although in recent years there has been a definite trend toward the use of thicker and therefore less porous coatings. Until a few years ago, the maximum thickness of commercial nickel coatings averaged 0.0002 inch, whereas at the present time thicknesses of 0.001 to 0.002 inch are commonly specified.[41] Incidentally, the

[39] Hudson, J. C., *Trans. Faraday Soc.*, 25, 233 (1929).

[40] Finkeldey, W. H., *Proc. Am. Soc. Testing Materials*, Part 1, p. 38, (1938).

[41] Hogaboom, G. B., *Inco (Internat. Nickel Co.)*, 13, No. 4, 12 (1936).

Table 20.—Atmospheric Corrosion of Nickel.

Location	Original Weight	Change in weight, grams			Tensile Properties After 6 yrs.		% Change in Tensile Properties		Remarks
		1 yr.	3 yrs.	6 yrs.	Tensile Strength	Elongation (%)	Tensile Strength	Elongation (%)	
Pittsburgh No. 1	560.76 564.43	−3.90 −3.86	−10.82 −10.71	−23.05 −22.79	68,700	36.7	−5.9(*1.3*)	−0.3(*1.8*)	Heavy dark film.
Altoona No. 2	565.49 565.60	−3.83 −3.95	−11.76 −12.04	−24.86 −25.48	67,300	36.6	−7.8(*1.3*)	−0.5(*1.4*)	Heavy dark film with patches of slight scale.
New York City No. 4	561.82 565.53	−5.01 −5.07	−12.48 −12.58	−24.46 −24.45	67,600	36.3	−7.4(*1.4*)	−1.4(*1.2*)	Smooth heavy film with slightly mottled appearance.
Rochester No. 6	561.22 566.87	−0.53 −0.54	−2.03 −2.06	−5.52 −5.76	71,500	36.5	−2.0(*1.4*)	−0.8(*1.9*)	Smooth mottled film.
Sandy Hook No. 5	561.51 562.28	−0.74 −0.74	−2.36 −2.39	−5.10 −5.14	72,000	37.0	−1.4(*1.2*)	+0.5(*2.3*)	Smooth slate-colored film.
Key West No. 7	564.13 559.16	−0.14 −0.14	−0.41 −0.41	−0.75 −0.75	72,950	36.7	−0.1(*1.2*)	−0.3(*1.8*)	Very light film, metallic luster.
La Jolla No. 9	563.82 563.36	+0.08 +0.10	−0.19 −0.19	−0.53 −0.57	72,900	36.3	−0.1(*1.3*)	−1.4(*2.6*)	Slight speckling of powdery scale, underlying tarnish.
State College No. 3	566.06 562.88	−0.12 −0.12	−0.39 −0.38	−0.97 −0.98	73,650	37.0	+0.9(*1.2*)	+0.5(*0.8*)	Very slight tarnish.
Phoenix No. 8	564.94 561.31	0.00 0.00	−0.06 −0.06	−0.09 −0.10	72,800	35.9	−0.3(*1.1*)	−2.4(*1.0*)	Slight tarnish.

Note: Italics denote maximum per cent difference due to chance.

domestic consumption of nickel anodes increased from 2,500,000 pounds in 1926 to 9,000,000 pounds in 1937, owing to the increased use of nickel in the automobile industry as well as the trend toward increased thickness of coating. For automobile parts nickel undercoatings for chromium plate are generally 0.001 inch in thickness, and may be as much as 0.0015 inch on bumpers.

The relation of porosity to coating thickness for nickel coatings reported in recent investigations is given in Figure 37.[3] These coatings are probably somewhat superior to the usual commercial product of this range of coating thickness, but the data indicate the advantage which has been obtained in going to heavier coatings. While coatings 0.0015 inch in thickness are practically non-porous in character, it is seldom in commercial practice that this thickness is obtained in the recessed areas of articles of irregular shape. The interposition of a thin coat of copper between two coats of nickel, though uncommon in American practice, is a practical method of reducing the number of pits in deposits of ordinary commercial thickness.[42]

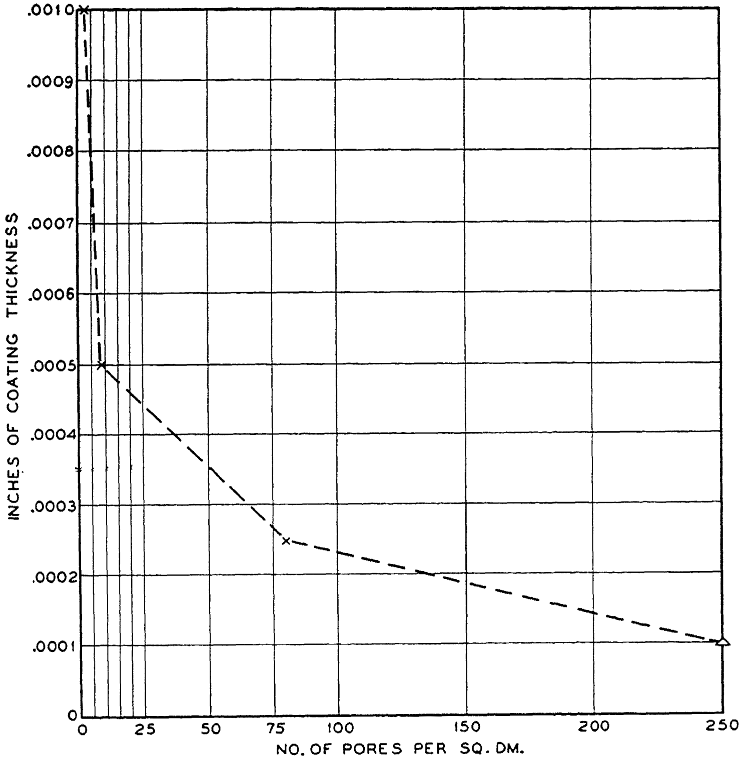


Figure 37.—Relation of Porosity to Coating Thickness for Nickel Coatings.[3]

Tests have indicated that electrodeposited nickel coatings 0.002 inch in thickness are equivalent in protective value to sprayed nickel coatings tenfold greater in thickness.[43]

The causes of porosity in nickel coatings are numerous and complicated and have been the subject of considerable study. Hydrogen is discharged in nickel plating, particularly in the early stages of deposition, and it has long been assumed that bubbles of this gas or of air have by adhering to the cathode given rise to pores. It has been suggested [44] that an accumulation of colloidal nickel compounds (probably hydrates) near the cathode is a factor favoring retention of hydrogen bubbles upon the cathode surface. It has lately been emphasized,[45] however, that gas bubbles are an incidental rather than a primary cause of porosity. Imperfections or impurities in the basis metal surface which are usually the foci of hydrogen evolution are areas which in themselves are not readily covered with the electrodeposit.

Among the principal causes of pitting are finely divided solid matter in suspension in the solution, foreign matter such as slag inclusions, buffing compounds in the surface of the steel, and a roughened condition of the surface. The suspended matter in the solution may be derived from anode slimes, precipitated basic compounds of iron, air-borne dust, calcium sulfate (from hard water used in preparation of solutions), lead sulfate (from lead linings of tanks), and finally, particles such as carbides, silica, etc., which are loosened in the surface of the basis metal in its preparation for electroplating. The marked reduction in porosity of nickel coatings obtained by the removal of solid particles by filtration of the plating solution is given in Table 21. Filtration (Series F) was accomplished by means of suction through a Büchner funnel using a fine filter paper. In one case (Series FF) filtration in this manner was preceded by boiling the solution with freshly precipitated nickel hydroxide. The specimens employed in this test were curved strips of steel.

Table 21.—The Effect of Filtration on Porosity.[45]

Condition of Solution		Average Thickness of Deposit (in.)	Average Thickness of Deposit (mm.)	No. of Specimens Tested	Average Porosity (No. pores per dm.^{2}) Concave Sides	Average Porosity (No. pores per dm.^{2}) Convex Sides
Not filtered	Series NF	0.001	0.025	5	30	9
Carefully filtered	Series F			3	6.2	0.9
Not filtered	Series NF	0.0006	0.015	5	86	51
Carefully filtered	Series F			3	10	2.6
Not filtered	Series NF	0.0002	0.005	5	230	152
Carefully filtered	Series F			3	113	66
Specially filtered	Series FF			9	32	25

---

[42] Cymboliste, M., *Trans. Electrochem. Soc.*, 70, 379 (1936).

[43] LaQue, F. L., *Internat. Nickel Co. Bull. T-13*, Dec., 1937.

[44] Macnaughton, D. J., Gardam, G. E., and Hammond, R. A. F., *Trans. Faraday Soc.*, 29, 729 (1933).

[45] Hothersall, A. W., and Hammond, R. A. F., *Trans. Electrochem. Soc., Preprint*, 73, 449 (1938). This excellent analysis of the causes of porosity is the principal source of the information given in the following paragraph.

As already mentioned the physical state of the cathode surface has an important bearing upon pitting in thin nickel deposits. Sandblasting or file-scratching of a polished steel surface prior to the deposition of coatings 0.00006 to 0.0002 inch in thickness has been shown to produce very marked increases in porosity. The fine-grained surface produced by etching steel anodically in concentrated phosphoric acid is more suitable than the relatively coarse-grained surface obtained in dilute sulfuric acid for the production of nickel coats of low porosity.[46]

The ordinary type of pores in nickel coatings which have been under discussion in the preceding chapters consist in microscopic channels extending through the coating to the basis metal. To be distinguished from pores are defects known as pits; these are craters of varying depth which may perforate the coating. While many of the conditions responsible for porosity may also give rise to pitting, a careful investigation of the matter has led to the conclusion[44] that pitting is associated with the presence of flocculated basic matter at the cathode surface. The prevention of pitting, then, involves such measures as filtration and the removal of organic impurities from the bath by oxidation with hydrogen peroxide, chlorine[47] or potassium permanganate.[48] It has been shown also, that pitting in baths of low acidity may be reduced by the introduction of sodium or potassium salts, and this result has been attributed to the stabilizing effect of alkali ions in preventing the flocculation of basic colloids.

Under certain plating conditions another type of defect, known as a blister pit, may appear. As the name implies, these are larger in size than ordinary pits and resemble blisters in appearance. Blister pits are probably due to small adherent gas bubbles which are gradually plated over during the deposition of the coating. There is evidence that in the formation of blister pits flocculent basic salts of relatively high electrical conductivity become attached to the surface of gas bubbles and that the electrodeposit is subsequently plated upon or grows over these colloid-coated bubbles.[49]

The practical importance of these considerations of the nature and causes of porosity and pitting lies in the possibility that a fuller knowledge of the factors involved will make possible the commercial production of nickel coatings of higher quality. An experimental study has shown that, by eliminating suspended matter from the solution and using specially prepared electrolytic iron or finely machined mild steel rod as basis metal, it is possible to obtain pore-free nickel deposits less than 0.0001 inch (0.0025 mm.) in thickness.[45] In view of the progress made in the field of electroplating in recent years it is not too much to expect that coatings of this quality will be obtained on a commercial basis.

It is well established, and is implied in the foregoing discussion, that the protective value of commercial nickel coatings in the atmosphere is a

[46] Burns, R. M., and Warner, C. W., U. S. Patent 1,658,222, (Feb. 7, 1928).

[47] Dorsey, F. M., *Ind. Eng. Chem.*, 20, 1094 (1928).

[48] Macnaughton, D. J., and Hothersall, A. W., *Trans. Faraday Soc.*, **26**, 163 (1930).

[49] Cymboliste, M., and Salauze, J., *Trans. Electrochem. Soc.*, **71**, 233 (1937).

function of their porosity and hence, at the present time, of their thickness. For instance, in the exposure tests conducted at the National Bureau of Standards in coöperation with the American Electroplaters' Society and the American Society for Testing Materials it was found that the thickness of the nickel layer is more important than any other factor.[50] The results obtained in this test at the end of 18 months of exposure are recorded in Table 22. The composition of the plating bath employed is that given earlier in the present chapter under the discussion of nickel plating solutions. The bath was operated at 35° C. at a current density of 2 amperes per sq. dm. in the procedure designated as "standard." Sets 4 and 7 were plated in this bath at 60° C., and 4 amperes per sq. dm. For Set 4 the pH value of the solution was 5.3 and for Set 7 the pH was 2.5.

Table 22.—Effect of Thickness of Nickel and Conditions of Deposition on Protective Value of Coatings.

Exposure 18 months. Per cent scores (see below).

Set No.	Procedure	Thickness inches × 1000	Key West (Marine)	New York City (Industrial)	Pittsburgh (Industrial)	Sandy Hook (Marine)	State College (Rural)	Washington (Suburban)	Average (6)	Marine Average (K.W., S.H.)	Industrial Average (N.Y., P.)	Suburban Average (S.C., W.)
52	Standard	0.25	10	17	8	10	31	35	19	10	13	33
5	Standard	0.50	25	30	20	27	70	82	42	26	25	76
1	Standard	1.00	67	67	36	62	87	86	68	65	52	87
2	Cath. pickle	1.00	54	67	36	64	91	87	68	59	52	89
3	Anode pickle	1.00	76	66	36	68	89	87	70	72	51	88
5	High temp., high pH	1.00	79	62	36	61	86	87	69	70	49	87
7	High temp., low pH	1.00	54	61	34	62	77	83	62	58	48	80
51	Std., not buffed	1.00	31	61	37	56	87	91	61	44	49	89
	Average (with 1.0)	1.00	60	64	36	62	86	87	66	61	50	87
6	Standard	2.00	79	86	52	79	96	94	81	79	69	95

Method of rating specimens:

Surface rusted (Per cent)	Rating	Percentage score
0	5	100
0–5	4	80
5–10	3	60
10–20	2	40
20–50	1	20
50–100	0	0

It is apparent from an inspection of the results in Table 22, which are based on over 100,000 individual ratings of specimens, that coatings with a thickness of only 0.00025 in. (0.006 mm.) afford very little protection to steel in exposures to outdoor atmosphere. Twice this thickness of coating, 0.0005 in. (0.013 mm.) is serviceable only in the mild atmospheres of rural or suburban localities, while coatings of 0.001 in. (0.025 mm.) are satisfactory except in highly industrial atmospheres. It will be seen that variation in the manner of electroplating is without any appreciable effect upon the protective value of the deposit.

---

[50] Blum, W., Strausser, P. W. C., and Brenner, A., *J. Res. Nat. Bur. Stds.*, **13**, 331 (1934).

Accelerated corrosion tests[51] and also outdoor exposure tests[52] have indicated that the corrosion resistance of a nickel coating deposited as a single layer is less than the resistance of a coating containing the same amount of nickel in the form of two layers with a film of copper sandwiched between. More recently the influence of a layer of copper on the protective value of nickel coatings was studied more extensively[50] by including composite nickel-copper-nickel coatings in the coöperative exposure test which has been described in the two previous paragraphs. The per cent variation in scores from those in Table 22 for pure nickel deposits of the same total thickness is given in Table 23. The copper layer was deposited from both cyanide and acid copper solutions without any significant difference in behavior being detectable. These results appear to be conclusive.

Table 23.—Effect of an Intermediate Layer of Copper on the Protective Value of Nickel Coatings.[50]

Per cent variation in scores from those of pure nickel deposits of the same total thickness.

Thickness (inches × 1000)	Key West	New York	Pittsburgh	Sandy Hook	State College	Washington	Average (6)	Marine Average	Industrial Average	Suburban Average
0.25	−7	+2	−2	−5	−18	−18	−8	−6	0	−18
0.50	−18	+15	−3	−8	+5	+4	0	−13	+6	+5
1.00 (Avg. of 9)	−42	+11	−13	−10	+2	+6	−8	−25	0	+4
2.00	−19	+8	−17	−1	+4	+4	−3	−10	−4	+4
Average	−21	+9	−9	−6	−2	−1	−5	−14	0	−1

It will be seen from Table 23 that the presence of copper is detrimental in very thin coatings in all locations and that corrosion is accelerated by copper in composite coatings of all thicknesses included in the test when exposed to marine or highly industrial atmospheres. On the other hand, the beneficial effect of copper is confirmed for the heavier coatings in rural, suburban and moderately industrial localities. It was found in this investigation that buffing of the copper layer improved somewhat the performance of the coating.

A preliminary layer of zinc or cadmium is sometimes used in nickel plating. As a rule, however, such coatings do not retain their bright metallic luster as well as do nickel coatings alone when exposed to corrosive conditions owing to a staining or filming of the surface by zinc or cadmium corrosion products. The protective value of composite zinc-nickel coatings is less than that of either metal alone, and cadmium under nickel has very little effect.[50]

---

[51] Baker, E. M., *J. Soc. Auto. Eng.*, **14**, 127 (1924).

[52] Thomas, C. T., and Blum, W., *Trans. Am. Electrochem. Soc.*, **48**, 69 (1925); **52**, 271 (1927).

Microstructure of Electrodeposited Nickel Coatings

The microstructure of electrodeposited nickel is similar to that of other electroplated coatings, although the grain size is usually much smaller, particularly in deposits obtained at low pH from solutions consisting entirely or in part of nickel chloride. Deposits from nickel sulfate baths of low pH, on the other hand, are somewhat coarse-grained, soft and ductile.[53] Raising the pH value (lowering the acidity) of the plating solution tends to refine the grain size and increase the hardness of the deposit. It has been observed, further, that alkali metal ions, and particularly ammonium ions, tend to harden nickel deposits.[54] At low temperatures and low current densities, the presence of chlorides in the plating solution has long been known by general experience to produce soft deposits; yet it has been shown that at high current densities and high temperatures the presence of chloride leads to hard deposits.[53] It is evident that nickel deposits of a wide range of hardness can be obtained by the proper adjustment of the bath and conditions of operation. A comparison of the Brinell hardness range of nickel and other electrodeposited metals is shown in Figure 38.[55]

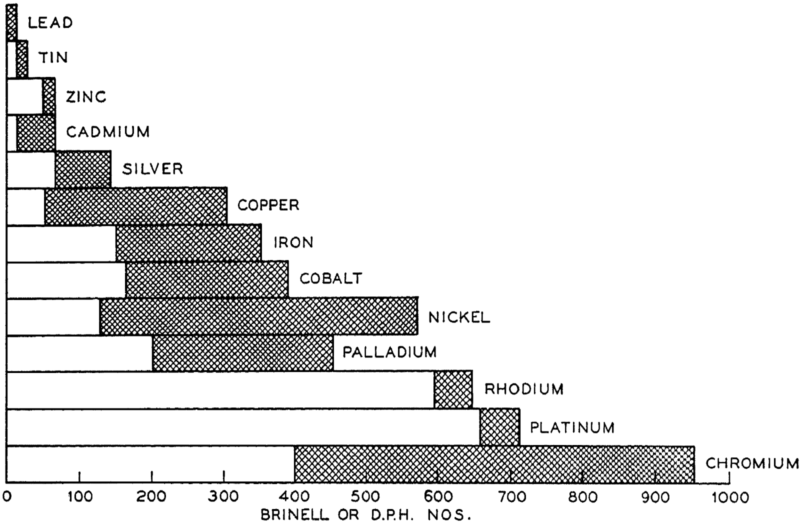


Figure 38.—Brinell Hardness Range of Various Electrodeposited Coatings.

Soft electrodeposited nickel possesses a pronounced fibrous structure with the grains elongated in the direction perpendicular to the surface of the base. This is shown in Figure 39 [56] for a deposit of the hardness range

---

[53] Blum, W., and Kasper, C., *Trans. Faraday Soc.*, 31, 1203 (1935).

[54] Macnaughton, D. J., and Hothersall, A. W., *Trans. Faraday Soc.*, 31, 1168 (1935).

[55] Hothersall, A. W., *Met. Ind. (London)*, 48, 115 (1936).

[56] Wesley, W. A., *Monthly Rev. Am. Electroplaters' Soc.*, (August, 1938).

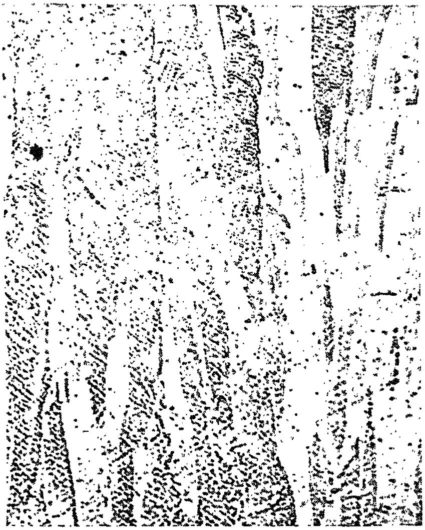


Figure 39.—Structures of Soft Electrodeposited Nickel.[56] Hardness Range 140-160 Vickers (×500).

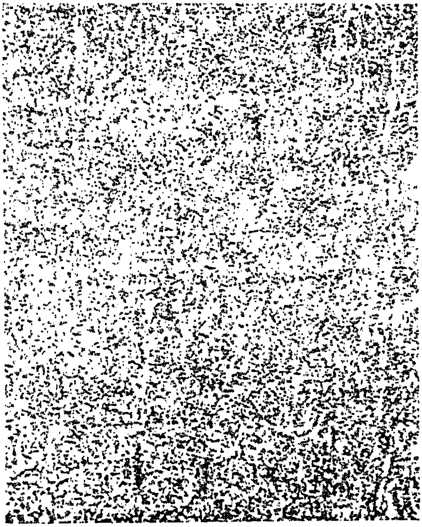


Figure 40.—Structure of Moderately Hard Electrodeposited Nickel.[56] (×500) Hardness: 230 Vickers.

140-160 on the Vickers scale obtained from the warm Watts type bath. Figure 40 illustrates the refinement in grain structure of a moderately hard nickel electrodeposit, and Figure 41 the structure, so far as it can be revealed, of a very hard deposit testing 350-400 in Vickers hardness. In the latter case the grain size is practically sub-microscopic, and in this and the moderately hard deposit the crystals were observed, by x-ray examination, to be oriented in a random fashion.

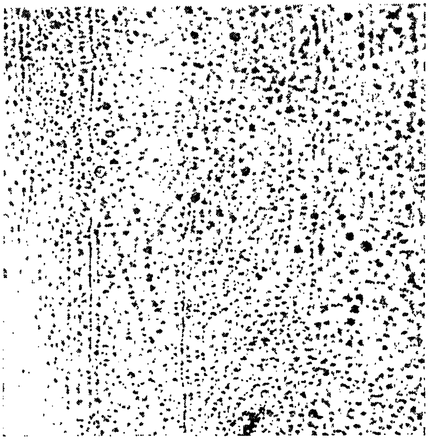


Figure 41.—Structure of Very Hard Electrodeposited Nickel.[56] 350-400 Vickers Hardness. (×500)

The relation of the structure and hardness of nickel deposits to bath composition and operation is still obscure. It has been suggested that the cause of small grain-size and high hardness obtained in solutions of high pH values is due to the interference with crystal growth exerted by colloidal basic nickel compounds.[44] While the Brinell hardness of ordinary nickel deposits may vary from 125 to 400, a hardness of 550 may be obtained by the addition of organic colloids to the plating bath.[54]

Related to structure of deposit is the tendency of certain hard, brittle nickel deposits to peel from the basis metal and curl in tight rolls. This tendency is a factor of importance affecting the adherence of the coating. Apparently such coatings are deposited in a highly stressed condition. It has been demonstrated, for example, that a tensile stress as high as 43,000 pounds per square inch may exist in a nickel coating which, being deposited on one side of a steel ruler, caused the ruler to bend into a bow, the coating being on the concave side.[57] The fact that the tension may be reduced by annealing at low temperatures has suggested that the phenomenon may be due to the deposition of hydrogen in the coating. Coatings which are very highly stressed are usually detected before they are put into service. Such coatings are usually more prone to failure under corrosive conditions than are similar ones not so stressed. Any corrosion between coating and base originating in pores or pinholes in the coating may serve to initiate peeling of the coat.

---

[57] Stoney, G. G., *Proc. Roy. Soc.*, **82**, (A) 172 (1909).

CHROMIUM COATINGS

Historical

The electrodeposition of chromium [58] was reported in 1854 by the German chemist Bunsen, better known as the inventor of the gas burner which bears his name. However, Geuther (1856) appears to have been the first to deposit the metal from a chromic acid bath. The chromic acid used in the experiments was precipitated from potassium dichromate with sulfuric acid and unquestionably contained a small percentage of sulfate. Geuther obtained "a coherent grayish-white coating with a metallic luster."

Sporadic and frequently unsuccessful attempts were made to repeat Geuther's experiments. It was not until 1905 that Carveth and Curry [59] explained the failures as being due to inadequate current densities, recognized the fact that the sulfate invariably present as an impurity is an essential feature of the bath, and advocated its intentional addition (preferably as sulfuric acid) in proportions up to one per cent. Interest was stimulated by this work and investigations became more frequent and more successful. Various sulfates and a few other salts and acids were substituted for sulfuric acid. Sargent [60] (1920) preferred chromic sulfate to sulfuric acid. Schwartz [61] (1923) employed chromium anodes with "Sargent's solution." It is interesting to note that most of the chromic acid baths studied since Geuther are identical in composition with the bath almost universally employed in present practice.

The slow progress made in the development of chromium plating can be attributed in large part to the little-recognized fact that bright chromium plate, which is now so widely applied, was virtually unknown and the type of deposit usually obtained was not particularly desirable. Investigators were more interested in electrowinning and electrorefining chromium than in electroplating it; and in order to secure maximum efficiency of metal deposition they usually employed high current densities and cold solutions, often chilled with ice. In consequence, the deposits were usually dull and rough, not unlike electrolytic zinc in appearance, and because of their extreme hardness were quite unsuitable for finishing operations.

In 1924, Haring [62] succeeded in consistently depositing a smooth, bright chromium plate with a mirror-like surface which required no buffing. He applied this coating to the intaglio plates used for printing money and stamps at the United States Bureau of Engraving and Printing. This first successful application of chromium plating was not due to any novelty insofar as the plating solution was concerned, but to discovery of the fact that bright chromium can be deposited consistently from the chromic acid bath provided that the current density is carefully maintained within relatively narrow limits, which are determined not only by the bath temperature but also by *the nature of the basis metal.* Since this time, the application of chromium plating has become widespread, and chromium plating practice has changed but little.[58] An extensive patent literature on the subject appeared during the early years of commercial development.[63] Perhaps the best known patent was that granted to Fink in 1926.[64]

---

[58] For an excellent account of the history, theory and practice of chromium plating see Haring, H. E., and Barrows, W. P., *Bur. Standards Tech. Paper,* **346**, June 10, 1927. Extensive use is made of this article in the present discussion.

[59] Carveth, H. R., and Curry, B. E., *J. Phy. Chem.,* **9**, 353 (1905); also *Trans. Am. Electrochem. Soc.,* **7**, 115 (1905).

[60] Sargent, G. J., *Trans. Am. Electrochem. Soc.,* **37**, 479 (1920).

[61] Schwartz, K. W., *Trans. Am. Electrochem. Soc.,* **44**, 451 (1923).

[62] Haring, H. E., *Chem. and Met. Eng.,* **32**, 692, 756 (1925).

The principal applications of chromium plating are to plumbing fixtures and automobile parts where a permanently lustrous finish is desired, and to printing plates, tools or machine parts subject to wear where a high degree of hardness is required. For articles which must be used at elevated temperatures, such as flat irons, chromium plating is superior to other metals. All these uses are now well known and established. In the thickness range in which it is generally applied, chromium plate affords but small protection against corrosion.

The high reflectivity of chromium has led to the use of chromium plating for reflectors for locomotive headlights and other similar applications. Although the reflecting power of polished chromium is considerably less than that of polished silver (70 per cent for $\lambda = 0.579\ \mu$ as compared with 93 per cent for silver under the same conditions), the ability of chromium to remain untarnished has led to its use for this purpose. More recently aluminum oxidized by a special process has become a competitor of chromium plating as a reflecting surface.

Theory and Practice of Chromium Plating

Extensive studies have been made in recent years of chromium plating solutions and their operation. Chromium deposits may be obtained from solutions of a variety of chromium salts [65] and also from chromic acid solutions containing small amounts of anions other than sulfates, *e.g.*, fluoride [66] and fluosilicate. It was found early in the industrial development of chromium plating, however, that the chromic acid-sulfate bath gave the most consistent and dependable results. This bath is now used almost universally in commercial practice. The simplest formula for this bath for general purposes is as follows: [6]

Acid		g./l	oz./gal.
Chromic (as CrO_3)	2.5 *M*	250	33
Sulfuric	0.025 *N* to 0.05 *N*	1.25 to 2.5	0.17 to 0.33

---

[63] Schneidewind, R., *Univ. Mich. Eng. Research Bull. No. 8*, (Nov., 1927).

[64] Fink, C. G., U. S. Patent 1,581,188, (April 20, 1926).

[65] Britton, H. T., and Westcott, O. B., *Trans. Faraday Soc.*, 27, 809 (1931); 28, 627 (1932).

[66] Hambuechen, C., U. S. Patent 1,544,451, (1925).

Somewhat higher chromic acid concentrations may be used for special purposes. Baths of the above compositions may be operated at a temperature of 45 to 55° C. (113 to 131° F.) and at an average current density of 10 to 30 amperes per square decimeter (93 to 280 amp./sq. ft.). Lead or steel anodes are generally employed, the former being preferable. For occasional and other than continuous use, lead alloyed with about 6 per cent antimony is more satisfactory than pure lead.[67] It is sometimes necessary to remove from lead anodes an accumulation of lead chromate and peroxide.

It will be seen from the range of composition of the solution given in the last paragraph that the sulfate content bears a definite relation to the chromic acid content. That is, the ratio of CrO_3 molarity to SO_4 normality ranges from 100 to 50, although a ratio of 200 works satisfactorily. These proportions of sulfate have been found most suitable and are subjected to close analytical control. According to one theory the function of sulfate ions is to permit the formation of a soluble divalent chromium salt from which chromium can be plated. In the electrolysis of chromic acid, chromium is reduced from the hexavalent state to the trivalent and probably electrodeposited from the divalent ion.[68] In the absence of sulfate (or other anion of a soluble chromic salt) there is formed on the cathode in pure chromic acid upon electrolysis a colloidal basic compound of indefinite composition and low solubility known as "chromium chromate." Precipitation of this substance blocks further reduction and prevents the deposition of chromium. The character of electrodeposited chromium varies widely depending upon the nature of the basis metal, the temperature of the plating bath and the current density employed. Three types of deposit have been distinguished,[66] namely, "dull" or "frosty," "bright" and "milky." Dull deposits may be satisfactory if a bright appearance and smoothness of surface are not required, but for most applications the bright deposit with its mirror-like finish which requires no buffing is essential. The milky deposit is thin, relatively soft and inadequate for most purposes. In order to obtain the bright chromium deposit consistently, it is imperative that all plating conditions be carefully adjusted and controlled.

The optimum average current density for the production of a bright deposit from a bath of given composition operated at a given temperature depends upon the nature of the metal which is being chromium-plated. In Figure 42 [58] typical curves for the plating range of a chromic acid-sulfate bath upon steel, nickel, copper and brass are shown. It will be seen that the range of current densities at which a satisfactory bright deposit can be obtained is greater at high than at low temperatures. The advantage from a plating standpoint of copper as an undercoating is indicated and has been confirmed in later work by others.[69] It is claimed that bright chromium deposits may be obtained over a wider current density range from chromic acid solutions in which the fluoride ion is substituted for the sulfate ion.[70]

---

[67] Baker, E. M., and Merkus, P. J., *Trans. Electrochem. Soc.*, **61**, 327 (1932).

[68] There is a difference of opinion on the last point. See Kasper, C., *Bur. Standards J. Res.*, **14**, 693 (1935); and also Liebreich, E., *Z. Elektrochem.*, 40, 73 (1934); Birükoff, N. D., Makariewa, S. P., and Timochen, A. A., *Korr. Metallschutz*, **11**, 172, 193 (1935); Mueller, E., *Z. Electrochem.*, **40**, 326, 344 (1934).

The throwing power of chromium plating baths is notoriously low, with the result that it is difficult to plate articles of irregular shape satisfactorily. Recessed areas are likely to receive little chromium and that which is deposited may be milky in appearance owing to the fact that the current densities in these areas fall outside the bright plating range illustrated in Figure 42. There seems to be little possibility of markedly improving the throwing power of the chromic acid plating bath by modifying its composition. The most favorable operating conditions for obtaining maximum throwing power are high temperature (55° C.) and high current density (35 amp./sq. dm.) coupled with low chromic acid and sulfate contents.[71]

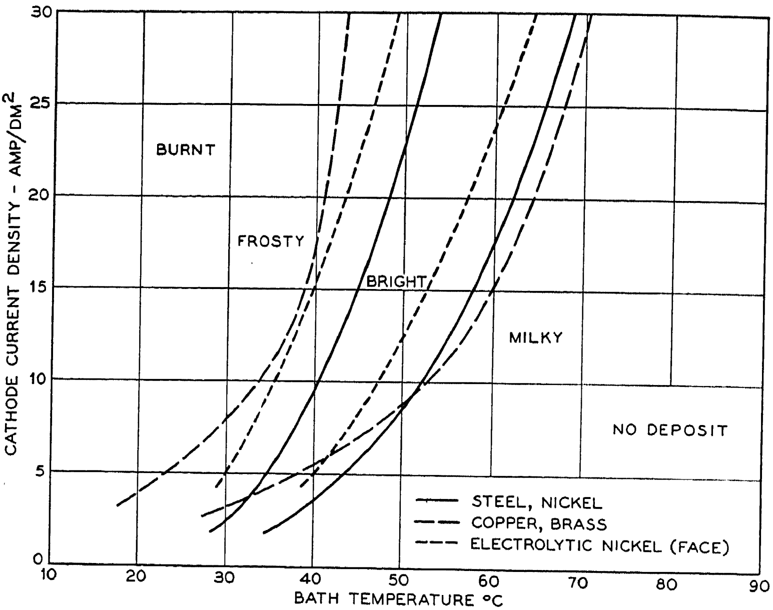


Figure 42.—The Effect of Basis Metal, Current Density and Temperature on the Character of Chromium Plating.

As would be expected a striking characteristic of chromium plating baths is their low cathode efficiency. This is rarely more than 20 per cent and is usually from 12 to 16 per cent for the production of bright deposits. The reduction of hexavalent chromium and the discharge of hydrogen gas accounts for the major portion of the current consumption.

---

[69] Lukens, H. S., *Trans. Am. Electrochem. Soc.*, **53**, 491 (1928); Cuthbertson, J. W., *Trans. Electrochem. Soc.*, **59**, 401 (1931).

[70] Perlenfein, A., *Rensselaer Polytech. Inst. Eng. Sec. 5, Bull.* **39** (1933); also Curschmann, E., and Heinrich, H., *Monthly Rev. Am. Electroplaters' Soc.*, **23**, 52 (Feb., 1936).

[71] Farber, H. L., and Blum, W., *Bur. Standards J. Res.*, **4**, 27 (1930).

The hardness of chromium coatings expressed in Brinell units is 500 to 900,[72] a range of values which is higher than that reported for electrodeposits of any other metal. More recently values up to 1200 on the Brinell scale have been determined.[73] Platinum and rhodium deposits of Brinell hardness values of 640 [74] and nickel up to 550 [54] have been the nearest approach by other metallic coatings to the hardness of chromium.

The microstructure of chromium coatings, which is reflected in their high hardness, reveals crystals so fine that their detection is difficult under an ordinary microscope. By means of electrolytic etching in hot chromic acid containing a small proportion of sulfuric acid it has been found that the deposits generally contain numerous inclusions of foreign material. This investigation [73] has shown furthermore that both the composition of the plating solution and the conditions of electrolysis exert a distinct influence on the structure and hardness of chromium deposits. The effect of current density and bath temperature upon Brinell hardness is shown, for example, in Figure 43.

Chromium deposits upon copper and nickel are somewhat more uniform in character than those upon steel. Studies [75] have shown that in the deposition of chromium upon steel surfaces the deposit appears initially upon cementite areas and then spreads rapidly to the ferrite within the pearlite areas. Chromium may be plated directly upon aluminum [76] and upon zinc and zinc alloys,[77] but such coatings do not provide a very high order of protection to these materials.

The commonly used undercoating for chromium plate, as already mentioned, is nickel. Until the development of bright nickel it was necessary to buff the nickel deposit before application of chromium in order to obtain the required high luster of the chromium finish. This operation has been the most expensive step in the process, and its elimination is reducing the cost of the chromium finish appreciably.

A recent development of interest is the production of black deposits of chromium.[78] These coatings, which have a pleasing appearance, are deposited from solutions of chromic acid containing a small addition of acetic acid at current densities of 80-150 amperes per square decimeter (about 750-1400 amp./sq. ft.). The temperature of the bath is maintained below 15° C. (59° F.). Black chromium plate may be plated directly on steel, nickel or brass, but because of its higher cost it is generally deposited on a nickel-bright chromium coating.

---

[72] Becker, E., *Giesserei*, **18**, 953 (1931).

[73] Cymboliste, M., *Trans. Electrochem. Soc.*, **73**, 353 (1938).

[74] Atkinson, R. H., and Raper, A. R., *J. Electrodepositors' Soc.*, **9**, 77 (1934).

[75] Ewing, D. T., Publow, H. E., and Tuttle, C. D., *Michigan State Coll. of Agri. Engg. Expt. Station Bull. No. 33* (1930).

[76] Work, H. K., and Slunder, C. J., *Trans. Electrochem. Soc.*, **59**, 429 (1931); Altmannsberger, K., *Chem. Zeit.*, **55**, 709 (1931).

[77] Anderson, E. A., and Reinhard, C. E., *Automotive Ind.*, **66**, 528, 542 (1932); Thompson, M. deK., and Jelen, F. C., *Trans. Electrochem. Soc.*, **63**, 141 (1933).

[78] Pollack, A., *Chem. Zeit.*, **59**, 56 (1935); Weis, A., *Oberflachtentech.*, **13**, 101 (1936).

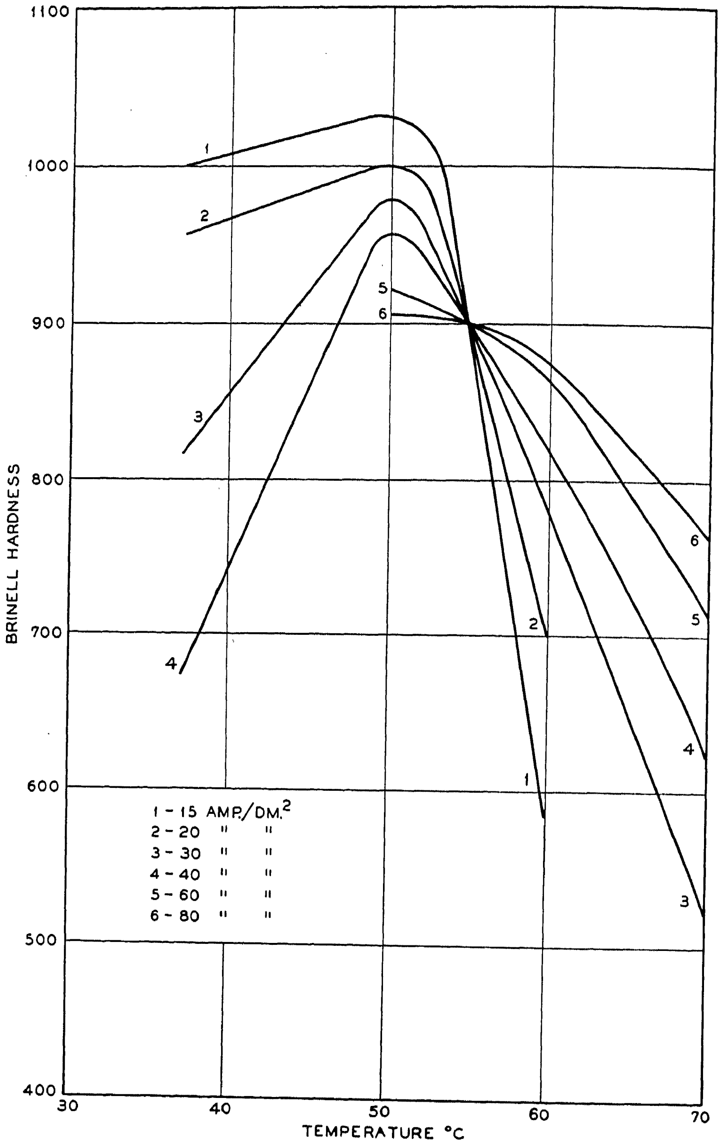


Figure 43.—The Effect of Current Density and Temperature of Bath Upon the Hardness of Chromium Plating.[73]

Chromium Cementation: "Chromizing"

A coating of chromium on iron may be produced by cementation in a manner analogous to that used for sherardizing. The parts to be treated are packed in a container with a mixture of 55 parts of chromium powder and 45 parts of alumina by weight and heated *in vacuo* or in an inert atmosphere, preferably hydrogen.[79] The material is usually heated to 1300-1400° C. (2370-2560° F.) for 3 or 4 hours in a molybdenum-wound furnace, although lower temperatures and shorter periods of heating may be used when less penetration is desired. Thus heating at about 1000° C. (1850° F.) for one hour will produce a casing about 0.004 to 0.005 inch in depth. The rate of penetration becomes accelerated above 1300° C., and when thicker coatings or higher concentrations of chromium are desired it is customary to operate in this temperature region. At a given temperature the depth of penetration is a linear function of time.[80] It is essential that oxygen and water vapor be excluded from the system, for otherwise at the high temperatures employed chromium is rendered inactive by the formation of a film of oxide which interferes with diffusion. Powdered ferrochromium has been used in place of chromium in chromizing.[81] While the process is usually carried out on finished or semi-finished steel articles another possible method of application is to produce a thick chromized coating on a bar or billet and then work these down to sheet, rod or strip stock.

The metals, chromium and iron, alloy very readily with one another. Although different investigators have reached varying conclusions concerning the equilibrium diagram of this alloy system, the fact that chromium readily goes into solid solution in iron is the essential and favorable condition for the chromizing process. The microstructure of a chromized iron sample is shown in Figure 44. The chromium is evidently in solid solution in the iron. The surface of a chromized metal is not exceptionally hard for it can be polished readily to a high luster. Iron or steel of low carbon content (0.10-0.20 per cent) can be chromized readily. High-carbon steels are difficult to treat unless their surfaces are previously decarburized by heating in hydrogen.[79] Ordinarily the chromium content of the diffused layer varies between 10 and 20 per cent. The behavior of a chromized metal upon heating is similar to that of a calorized material. The chromium diffuses deeper into the metal as the heating is continued and the chromium content of the surface layer is gradually reduced. For example, the chromium content of the surface layer on an iron sample which was treated for three hours at 1350° C. has been reported to be 10.4 per cent. By heating a similarly treated rod for three hours more in hydrogen the chromium content of the surface layer was reduced to 7 per cent.[79] The dimensions of iron or steel articles are not appreciably changed by the chromizing treatment.

---

[79] Kelley, F. C., *Trans. Am. Electrochem. Soc.*, 43, 351 (1923); U. S. Patent 1,365,499 (Jan. 11, 1921).

[80] Kelley, F. C., *Am. Soc. Metals Handbook*, 1938.

[81] Laissus, J., *Compt. rend.*, 180, 2040 (1925).

The corrosion resistance of chromized steel is somewhat similar to that of high-chromium steels, although no very extensive studies appear to have been carried out. Chromized steel is resistant to steam and to atmospheric conditions. In the salt-spray test chromized iron resisted corrosion as well as sherardized specimens and after a month's exposure gave only slight evidence of attack. Specimens chromium-coated by this method were found to have a decided resistance to attack by dilute nitric acid, but were very readily attacked by dilute hydrochloric and sulfuric acids. It has been suggested that chromized nickel steel will withstand erosion exceptionally well when used in the construction of turbine buckets.[79]

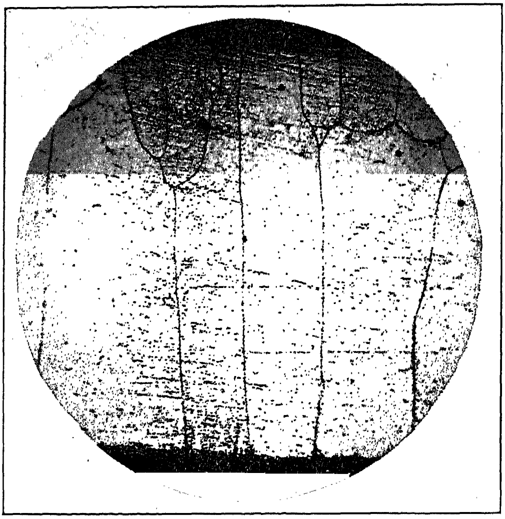


Figure 44.—Structure of a Coating Produced on Iron by "Chromizing," Heated for 4 Hours at 1350° C. ×50. The Upper Edge Corresponds to the Outer Surface of the Coated Material.[80]

Owing to the marked advances which have been made in chromium plating and in the development of a large variety of corrosion-resistant alloy steels, the chromizing process has not enjoyed the commercial use which otherwise would have been warranted by the quality of the product.

The Performance of Chromium-Plated Coatings

It is well known that a chromium surface upon exposure to air is immediately coated with an extremely thin and invisible oxide coating which protects the metal indefinitely from further attack. When physically injured this coating repairs itself. In the absence of oxygen and particularly if chlorides are present at the same time, the film on chromium is destroyed and the metal may suffer attack.

Electroplated chromium coatings in the thickness employed industrially are porous and often contain a network of fine cracks. By plating copper on chromium coatings it is possible to reveal the existence and the location of pores and cracks in the coating, the copper being deposited on these areas and not on chromium. The result of this experiment is shown in Figure 45.[82] Cracking is more likely to occur and to be more pronounced in thick coatings than in thin ones. A careful study [83] of the porosity of chromium coatings has shown that very thin coatings contain round pores which decrease in prevalence with increasing thickness of coat. Further increase in weight of coating is usually accompanied by the formation of cracks. There appears, therefore, to be an optimum thickness of coating (0.00002 to 0.00003 inch) which affords maximum protection. Changes in composition of the plating bath appear to have little effect on porosity,

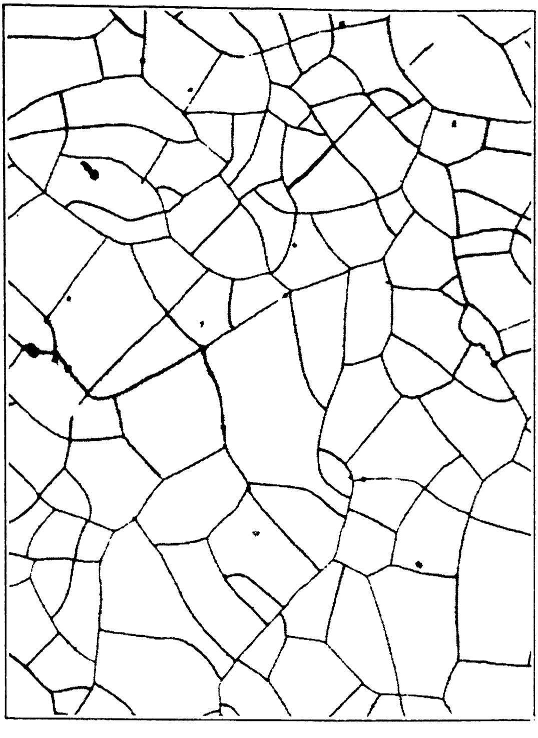


Figure 45.—Cracks (Lines) and Pinholes (Spots) in 0.00011-Inch Chromium Coating on Nickel Brought out by Copper Plating. ×100.[82]

---

[82] Gillett, H. W., (Abstract of a lecture by W. Blum) *Metals and Alloys*, 2, 365 (1931).

[83] Blum, W., Barrows, W. P., and Brenner, A., *Bur. Standards J. Res.*, 7, 697 (1931).

while increasing the bath temperature from 45 to 65° C. was found to result in a marked decrease in porosity especially in thick coatings. It is the existence of pores and cracks in chromium deposits that accounts for their low protective value when used alone. When applied to brass exposed to corrosive conditions chromium coatings often become filmed with a brownish layer of corrosion products derived from the substrate. Applied directly to steel, chromium coatings develop pinhole rusting upon outdoor exposure. Consequently it has become the universal practice in the use of chromium plating to apply an undercoating, usually nickel, for protective purposes, and to employ a thin veneer of chromium on top of this for appearance.

Mention has previously been made in the section dealing with nickel coatings of the jointly-sponsored systematic atmospheric corrosion test on nickel coatings. Included in this test were specimens coated with chromium and composite coatings of nickel and of nickel-copper, cadmium and zinc with chromium as an outer layer.[50] The chromium coatings were deposited from the standard chromic acid-sulfate baths (with some variation both in concentration and in ratio of CrO_3 to SO_4). Nickel coatings upon which chromium was plated were previously buffed. The temperature of the chromium solution was varied from 35 to 65° C. (95 to 149° F.) and the current densities chosen to yield bright deposits at about 12 per cent cathode efficiency. In this connection it is of interest to note that the coatings produced at 35° C. were consistently about 15 per cent superior to those produced at the higher temperatures. Changes in the concentration of chromic acid did not affect the value of the coatings, but a decrease in sulfate content (*i.e.*, an increase in the ratio CrO_3 to SO_4) made a consistent improvement of about 20 per cent in coatings deposited at 45° C. and 16 amperes per sq. dm. The performance of the chromium finish exposed to various outdoor atmospheres in this exposure test is given in Table 24.

Table 24.—Protective Value of Various Composite Coatings with Outer Layer of Chromium.[50]

(Total thickness 0.001 inch including 0.00002 in. chromium)
18 months' exposure. Per cent scores.*

Set Number	Undercoat	Key West	New York	Pittsburgh	Sandy Hook	State College	Washington	Average (6)	Marine Average (K.W., S.H.)	Industrial Average (N.Y., P.)	Suburban Average (S.C., W.)
101	Ni 0.001	54	69	23	47	100	99	65	51	46	100
121	Zn 0.0005, Ni	81	47	20	65	85	80	63	73	34	83
123	Cd 0.0005, Ni	71	63	22	79	97	93	71	75	43	95
124	Zn 0.0002, Cu 0.0003, Ni	75	60	24	81	87	97	71	78	42	92
125	Cd 0.0002, Cu 0.0003, Ni	63	59	29	77	99	95	70	70	44	97
137	Cd 0.0005	38	67	64	78	93	87	71	58	66	90
138	Zn 0.0005	38	79	77	88	95	79	76	63	78	87

* For method of rating see Table 23.

The most striking feature of the results given in Table 24 is the excellent performance of all the coatings in the suburban atmospheres in contrast to the poor showing in the industrial regions. It is not surprising that the coatings gave evidence of failure in marine localities for it is general experience in the automobile field that the salt content of seaside atmospheres tends to cause rusting of nickel-chromium finishes. These findings are in agreement with the results for nickel coatings alone reported in Table 23 and indicate that the performance of the finish is determined largely by the behavior of the nickel component of the coating. Incidentally it has been estimated [50] that plated coatings which furnish satisfactory protection in such localities as State College and Washington for a year or more should last almost indefinitely under normal household or office conditions.

It is rather difficult to explain the variable results obtained in this investigation with intermediate zinc and cadmium coats. In general there appears to be no consistent advantage in composite coatings of this character and in many cases detrimental effects are obtained. Where chromium is applied directly over zinc or cadmium the finish develops a dull appearance after a few months' exposure, resembling the behavior of thin chromium coats on brass alluded to previously. Chromium coats 0.0002 inch in thickness applied to steel and exposed in the above test rusted badly within a few months and were generally inferior to specimens with 0.00025 inch of nickel or of copper and nickel.

Chapter 10

Coatings of Copper, Lead, Aluminum and Miscellaneous Metals

COPPER COATINGS

Copper is not ordinarily recommended as a coating for the protection of iron or steel against corrosion. An article completely coated with copper, if the coating were intact at all points, would, of course, resist corrosion as effectively as a piece of solid copper, but only so long as the coating remained intact. The cathodic behavior of copper with respect to iron when the two metals are in contact and wet with an electrolyte is more marked than the behavior of nickel in this respect. Copper, however, does not have the pleasing appearance of nickel and lacks the ability to retain a high polish, both of which are properties that favor the use of nickel as a coating metal in spite of its cathodic nature with respect to iron. As a general rule, copper coatings are used for other purposes than protection from atmospheric corrosion.

Coatings of copper may be deposited very readily by electroplating, by metal spraying and by mechanical coating processes. In addition, some special methods, as noted below, have been proposed.

Electroplated Copper Coatings

Firmly adherent coatings of copper can readily be deposited electrolytically. The two solutions in common use today, which have been used for a good many years, are the acid sulfate and the alkaline cyanide solutions. Recently a modification of the alkaline cyanide bath obtained by the addition of Rochelle salt (sodium potassium tartrate) has been shown to have desirable characteristics. Copper-plating by means of the acid-sulfate bath is limited somewhat, since this solution cannot be used for plating directly upon iron. The "spongy" copper deposited on the surface of the iron upon immersion in copper sulfate solution prevents subsequent deposition of an adherent coat. For coating iron or steel, therefore, the cyanide solution must be used, at least at the start, although it has been stated[1] that copper can be plated directly upon iron provided the iron has been covered with a film of arsenic by being dipped into a solution of arsenic trioxide in concentrated hydrochloric acid. The alkaline cyanide plating bath, however, is generally a much more convenient means of copper-coating iron and steel than is such a solution of arsenic. A copper plating bath containing a complex sodium-copper oxalate salt known as disodium diaquo-dioxalatocupriate has been proposed as suitable for plating copper directly on steel.[2] Copper may be deposited from solutions of a variety of other copper salts, for example, from alkaline copper iodide solutions, forming in this case deposits which under some conditions contain iodine (or iodide).[3] Baths of this type, however, are of no commercial importance.

---

[1] Watts, O. P., *Trans. Am. Electrochem. Soc.*, 35, 265 (1919).

The acid-copper bath consists essentially in a solution of copper sulfate containing sulfuric acid, the proportion of the two constituents varying over fairly wide limits. For example, 150 to 240 grams per liter of $CuSO_4 \cdot 5H_2O$ (20-32 oz./gal.) and 50 to 75 grams of sulfuric acid per liter (6.7 to 10 oz./gal.) is a suitable concentration range for the production of satisfactory coatings under the ordinary conditions of operation.[4] Current densities up to 10 amperes per square decimeter (93 amp./sq. ft.) may be employed at ordinary temperatures, while at 45° C. (113° F.) double this current density is practical. Usually, however, somewhat lower current densities are used in copper plating. Addition agents, such as glue and more particularly phenol-sulfonic acid, have been recommended[5] for use in the acid bath when thick, smooth, fine-grained deposits are desired. Phenol up to 10 grams per liter may be used to produce smooth, hard and ductile coatings.[6] The cathode efficiency of the acid-sulfate-copper bath is generally in the neighborhood of 100 per cent. Copper anodes of high purity are readily available in either the electrolytic, cast or rolled forms, the latter being usually the most satisfactory.

The alkaline copper cyanide solution consists principally of the complex salt $Na_2Cu(CN)_3$ with varying amounts of carbonate and hydroxide. A typical commercial formula[4] for this bath contains 22.5 grams per liter of cuprous cyanide (3 oz./gal.), 34 grams per liter of sodium cyanide (4.5 oz./gal.) and 15 grams per liter of sodium carbonate (2 oz./gal.). The bath is usually operated from 30-40° C. (86-104° F.) and at current densities from 0.3 to 1.5 amperes per square decimeter (2.8-14 amp./sq. ft.). The cathode efficiency is from 50-90 per cent. Owing to the small dissociation of the complex copper cyanide ion $[Cu(CN)_3]^-$ the concentration of cuprous ions in the bath is very low. For this reason the alkaline cyanide bath possesses good throwing power. Deposits obtained from the bath are fine-grained.

The use of Rochelle salt in alkaline copper cyanide solutions permits the use of appreciably higher current densities.[7] The optimum composition for this bath is:

---

[2] Fink, C. G., and Wong, C. Y., *Trans. Electrochem. Soc.*, **63**, 65 (1933).

[3] Schlötter, M., Korpiun, J., and Burmeister, W., *Z. Metallkunde*, **25**, 107 (May, 1933); see also Schlötter, M., *Trans. Faraday Soc.*, 31, 1177 (1935).

[4] Blum, W., and Hogaboom, G. B., "Principles of Electroplating and Electroforming," 2nd ed., New York, McGraw-Hill Book Company, 1930.

[5] Ollard, E. A., and Perring, J. W., *Met. Ind. (London)*, **45**, 277, 423, 519 (1934).

[6] Hull, R. O., and Blum, W., *Bur. Standards J. Research*, **5**, 767 (1930); Hothersall, A. W., *Electroplaters and Depositors Tech. Soc. Preprint*, March, 1931.

[7] Graham, A. K., and Read, H. J., *Metal Ind. (N. Y.)*, **35**, 559, 617 (1937); **36**, 15, 77, 120 (1938).

Substance	Ounces/gallon	Grams/liter
Cuprous cyanide	3.5-5.5	26.2-41.2
Sodium cyanide	4.6-6.8	34.5-51
Free cyanide	0.75	5.6
Rochelle salt	8.0	60.
Sodium carbonate	4.0	30.

The pH of this mixture is 12.7.

The bath is operated in the temperature range 140-190° F. (60-88° C.) at cathode current densities from 20-90 amperes per square foot (2.16-9.7 amp./sq. dm.). When lustrous deposits are desired, as in plating die-castings prior to coating with nickel and chromium, the bath concentration is maintained at the lower values which are proposed.

Structure of Electroplated Copper Coatings

The microstructure of electrodeposited copper may be described in some detail since it is typical of many features common to electroplated coatings. For example, electrodeposits of copper usually consist in columnar or finger-like crystals arranged perpendicularly to the surface of deposition, that is, parallel to the direction of current flow. This is shown in Figures 46 and 47. The grain size and hence the hardness and strength of the deposited coating depends upon several different variables of deposition. For instance, an increase in current density results in a smaller grain size as well as a more irregular structure, a condition usually accompanying higher strength and hardness. Copper deposits made by use of cyanide solutions have a very fine grain size. Likewise addition agents, usually of a colloidal nature, in a plating bath aid in producing a very small grain size. Some of the colloidal matter is carried to the cathode where it obstructs the grain-growth of the deposit in which it is incorporated. The fine fibrous structure produced by the presence of colloids has been shown to be much harder than the large columnar crystalline deposit obtained in the simple acid sulfate bath.[8]

Addition of lead in amounts of 0.1 to 0.01 gram per liter to alkaline copper cyanide baths improves the brightness of the deposit markedly, the structure of the deposit being dense, compact and slightly banded.[9] Fractional percentages of lead are codeposited with copper in this instance. The banded structure appears to be associated with a fluctuation in deposition potential resulting in periodic deposition of the metal. Evidence has been educed [10] to show that "brightness" of deposits is related to the perfection of the orientation of the crystallites of the deposited metal. Very possibly the brightness of copper deposits induced by small amounts of lead may be the result of an alternate deposition of foreign matter (basic salts or lead) and oriented copper.[9]

---

[8] Macnaughton, D. J., and Hothersall, A. W., *Trans. Faraday Soc.*, **31**, 1168 (1935).

[9] Meyer, W. R., and Phillips, A., *Trans. Electrochem. Soc.*, **73**, 377 (1938).

[10] Schlötter, M., *Korr. Metallschutz*, **5**, 16 (1929); Wood, W. A., *Trans. Faraday Soc.*, **31**, 1248 (1935).

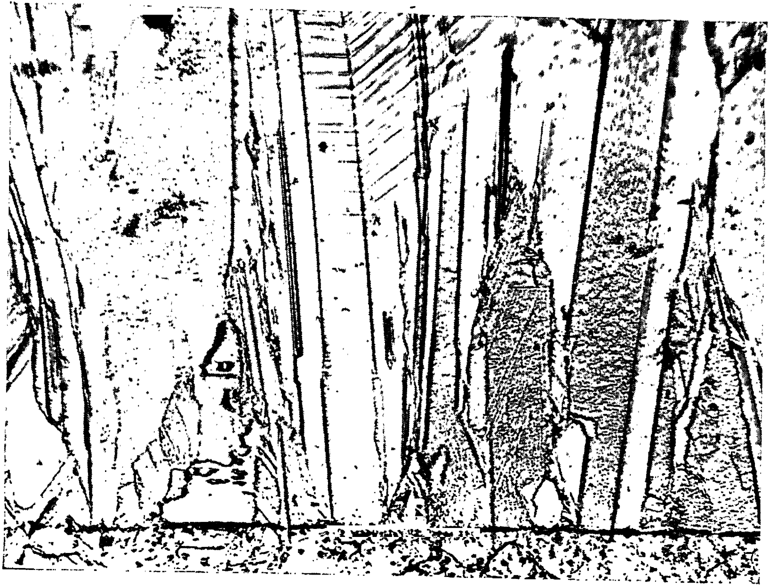


Figure 46.—Columnar Crystal Structure of Deposit Perpendicular to Surface of Deposition.[9]

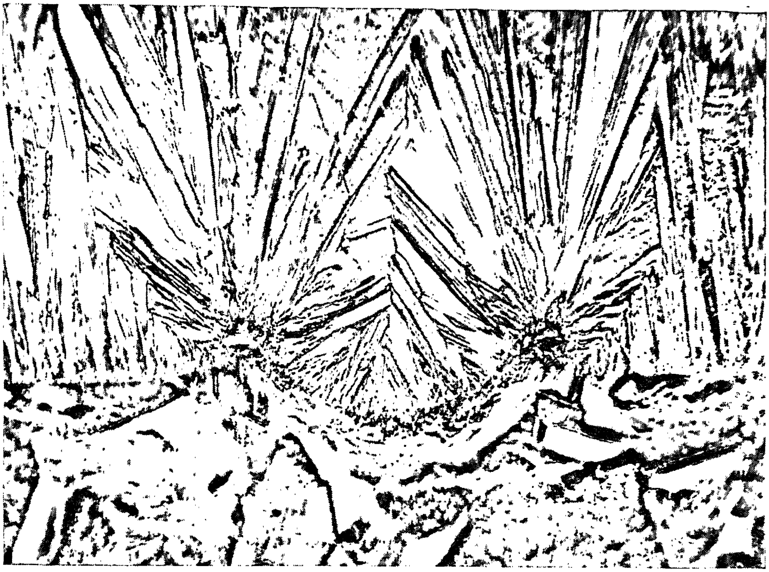


Figure 47.—Orientation of Crystals Deposited upon a Scratch in Basis Metal. Acid Copper Solution. Current Density 1 amp. per. sq. dm.[9]

Upon annealing electrodeposited copper there is usually a complete recrystallization of the metal. It would appear that the copper layer as deposit is not in a state of structural equilibrium but rather in a condition somewhat akin to cold-worked metal. This condition of electrodeposited metals with respect to internal stresses is probably of some significance in accounting for the hardness of such materials.[11]

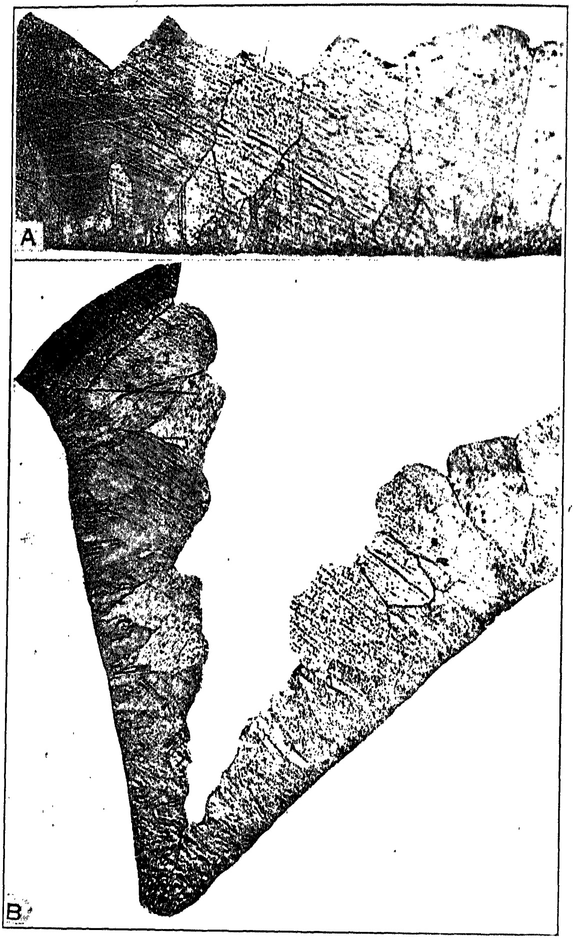


Figure. 48.—Variation in Coating Thickness of Electrodeposited Copper Depending on Contour of Surface. ×150. [Blum, W., Holler, H. D., and Rawdon, H. S., *Trans. Am. Electrochem. Soc.*, 30, 159 (1916)].

The uniformity in thickness of an electroplated coating depends largely upon the shape of the article plated. As is shown in Figure 48 the thickness of a copper coating at the base of a depression such as a V-groove may be not more than one-quarter the average thickness of the coat.

---

[11] Macnaughton, D. J., *J. Iron Steel Inst.*, 109, 409 (1924).

Adhesion of Electroplated Copper Coatings

The adherence of electroplated coatings is a matter of great practical importance. Unlike coatings produced by hot-dipping there is usually little if any diffusion of electroplated coatings into the basis metal. It is obvious, of course, that the surface to be plated must be clean if good adherence is to be obtained; the presence of oxides, sulfides, and extraneous materials such as grease may reduce adherence to the point where the coating peels from the surface. As has been pointed out in Chapter 2, deposits adhere more firmly to roughened surfaces because of the greater opportunity of physical anchorage which is thereby provided. That the removal of the disturbed or "disorganized" surface layer of a metal is often conducive to a higher degree of adherence is evident from experiments[12] in which copper was deposited on copper surfaces which had been etched with acid following the ordinary chemical cleaning. In this case it was found that the crystals in the plated layer were simply extensions of the surface crystals of the base, that is, it would appear that the strength of the bond between coating and base metal must approach in magnitude that existing between atoms in a solid. When, however, the base metal was merely cleaned without being etched, the deposited layer was firmly adherent, but without any evidence in its structure of having been influenced by the structure of the base metal. It is of interest to note that in the case of copper which had been cold-rolled so that the crystalline structure throughout the sheet was considerably disturbed and broken, the structure of the deposited layer on an acid-cleaned specimen showed only very slight evidence of any tendency to "repeat" the structure of the base.

Presumably the continuation of the microstructure of the basis metal in the electrodeposit is favored by relatively large crystals in the basis metal and conditions of plating which are conducive to the deposition of crystals of similar size. Interference with crystal growth by the inclusion of foreign ions, atoms or molecules tends to produce fine-grained deposits incapable of following the pre-existing crystal structure of the substrate. Recent studies[13] have shown that electrodeposited copper (and to some extent nickel and tin) may continue the microstructure of other metals when the deposit and basis metal belong to the same crystal system over a range of differences in lattice parameters, and even in some cases when deposit and basis metal belong to different crystal systems. In Figure 49 are shown examples of the continuation in electrodeposited copper of the crystal structures of certain specimens of rolled copper, nickel and silver.

---

[12] Blum, W., and Rawdon, H. S., *Trans. Am. Electrochem. Soc.*, 44, 305 (1923).

[13] Hothersall, A. W., *Trans. Faraday Soc.*, 31, 1242 (1935).

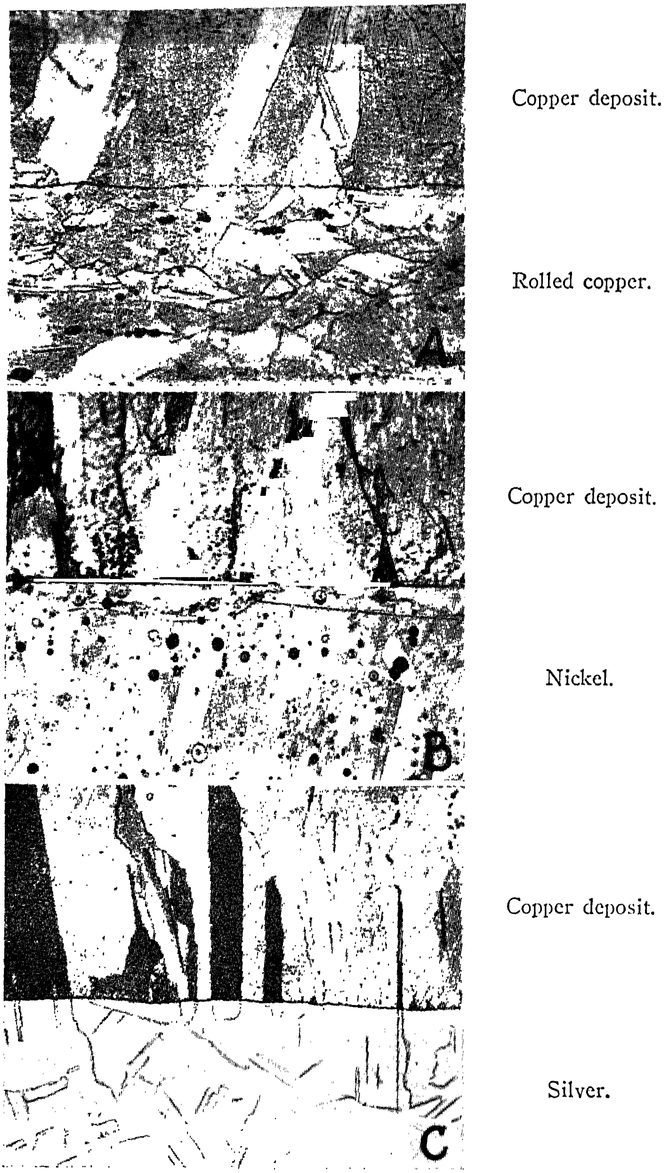


Figure 49.—Continuation of Structure of Basis Metal in Electrodeposited Copper.[13]

A. On Rolled Copper (X 133).
B. On Annealed Nickel (X 66).
C. On Annealed Silver (X 133).

Use of Electroplated Copper in Selective Carburization of Steel

It is often necessary in the case-hardening of steel parts that portions be left in their initial or relatively soft condition to allow machining to be done in such parts or to enable the piece to be straightened after hardening. Copper coatings play an important part in this process. Those portions of the surface which are to remain soft are electroplated with copper before the steel parts are packed in the carburizing mixture. This may be accomplished either by plating the entire surface with copper, usually in an alkaline cyanide bath, and then removing it mechanically from the areas to be hardened; or by coating the areas to be hardened with a baked japan or "stopping-off" compound, and then plating the bare surfaces to be protected, the organic finish being later burned off in the carburizing operation. At the close of the carburizing treatment, it is found that the presence of the copper layer has prevented carburization of the underlying steel and hence such parts do not harden appreciably when the piece is heated and quenched.

Copper applied by the metal-spraying process has been found to be effective in protecting against carburization.[14] Such a layer must be somewhat thicker than one which is electroplated, since the metal-sprayed layer may be slightly porous. The process is to be recommended because of the ease with which it can be used in applying a copper layer to a few spots, here and there, on an article to be carburized. It is a very simple matter to localize the deposit. Other conditions have favored the use of electroplating, however, and the metal-spraying process has not, as yet, found application in commercial carburizing plants in this country.

It is generally agreed that any coating that will prevent the access of the carburizing gas (carbon monoxide) to the underlying steel will answer the purpose.[15] Copper is the most useful of the metals, however. Nickel coatings, for example, are not suitable for the purpose as the carbon monoxide readily permeates them and carburizes the steel beneath. Cobalt would be expected to behave similarly and the melting points of the other coating metals commercially available are so much lower than the temperature used in carburizing as to be of no value. In practice, various kinds of non-metallic cements and pastes, sometimes containing powdered metals, are used.[16] They are not so dependable, however, as copper plating.

A layer of copper 0.005 inch thick is generally considered sufficient for practically any purpose. Studies have shown [17] that thinner coatings, for example, 0.0005 inch, will prevent carburization for periods up to 12 hours (at 1700° F.) and markedly retard penetration of carbon into the protected area for longer periods of treatment.

---

[14] Guillet, L., and Bernard, V., *Rev. Métal,* **11,** 752 (1914); *Iron Age,* **95,** 304 (1915).

[15] McCullough, J. C., and Reiff, O. M., *Ind. Eng. Chem.,* **16,** 611 (1924).

[16] Galibourg, J., and Ballay, M., *Rev. Métal,* **19,** 222 (1922).

[17] Vanick, J. S., and Herschman, H. K., *Trans. Am. Soc. Steel Treat.,* **4,** 305 (1923).

Mechanical Copper-Coating Process

The coating of steel with copper by use of the molten metal has been the subject of active investigation since the early part of the last century.[18] The difficulties attendant upon the high temperature necessary in using molten copper have precluded the use of the simple hot-dipping process.

The two metals alloy quite readily although they are not completely miscible in the molten state. Copper, at a temperature just below its melting point (1083° C., 1981.4° F.), can hold in solid solution approximately 3 per cent of iron. At the same temperature, iron dissolves approximately 8 per cent of copper. In both cases, the limit of solid solubility of one metal in the other decreases, as the temperature is lowered, to considerably less than one per cent at room temperature. Most alloys of the two metals therefore will consist of two constituents which are the two solid solutions, the relative amount of each constituent depending upon the composition.

In brief, the mechanical method which has been developed for coating steel with copper is to prepare a composite or duplex billet or ingot having a steel center and a copper casing, which is then rolled or drawn down to the desired shape. No unusual difficulties have been experienced in rolling such a composite billet, and the copper coating which results is much more impervious than an electrodeposited one of the same thickness.

Different methods have been proposed for the preparation of the duplex billet. According to one method described for "copper clad" steel,[19] the properly cleaned steel billet is heated red-hot and then momentarily immersed in a hot bath of molten copper to form a very thin uniform alloy layer over the entire surface, after which molten copper at a much lower temperature is cast around the billet. The casting is accomplished by means of a special mold, which, with the billet inside, is immersed in the bath of molten copper.

In order to minimize the formation of an alloy layer between the two metals, the "copper-weld" process was developed. This method consisted in electroplating the cylindrical steel billet with copper and then enclosing it in a neatly fitting cast-copper tube.[18] After luting the crevices at the end to prevent access of air, the billet was heated to approximately 950° C. (1740° F.) and then worked into the desired shape. An earlier and somewhat similar process [20] consisted in dipping the steel billet in molten copper to form a thin layer over the surface and then adjusting the copper sleeve and working it into shape as just described.

The method of casting copper directly around a hot steel billet enclosed in a suitable mold [21] is the simplest and is used commercially today. The composite billet can readily be worked mechanically at a temperature of 900° C. (1650° F.). The properties of the finished coated product do not

---

[18] Handy, J. O., *J. Ind. Eng. Chem.*, **5**, 884 (1913).

[19] Tassin, W., *Proc. Am. Soc. Testing Materials*, **10**, 280 (1910).

[20] Eldred, B. E., *Am. Machinist*, **30**, 474 (1907).

[21] Silverman, A., *Discussion, Trans. Am. Inst. Mining Met. Eng.*, **60**, 370 (1919).

INDIAN INSTITUTE OF SCIENCE LIBRARY BANGALORE

appear to be adversely affected by any increased alloying of the copper and iron which may result from this method. Brass and cupronickel may also be used for coating steel by this method.

Most of the steel coated with copper in this way is made into wire. The combination of high electrical conductivity and high tensile properties make this material a very useful one. The amount of copper used is dependent upon the desired conductivity of the finished wire. Such wire is usually designated in terms of the conductivity of a copper wire of the same size, for example, "30 per cent and 40 per cent conductivity." It is possible to obtain a minimum copper thickness at any point around the wire of 10 per cent of the wire radius on the 30-per cent grade and 12.5 per cent on the 40-per cent grade.[22]

Some use has also been made of copper-coated wire in screen cloth. Some copper-coated sheets rolled from a composite bloom have been made and used to a very limited extent for spouting, eaves-troughs and the like. Its use for bullet jackets has given very encouraging results. During the war, instead of the usual cupronickel bullet jacket, the Germans developed one made from a soft steel sheet coated with cupronickel by a process similar to that described above.

Miscellaneous Copper-Coating Methods

Richards[23] has described a method for coating steel with copper in which the copper is reduced from the oxide and melted *in situ,* that is, on the surface to be coated. The reduction of copper oxide by reducing gases, such as carbon monoxide or hydrogen, begins at a relatively low temperature, for example, as low as 130° C.[24] A mixture of powdered copper and copper oxide in crude oil ground to the consistency of a light varnish was applied to sheet steel while cold by means of rolls much like the inking rolls on a printing press, and the coated sheets were then conveyed by a chain conveyor into a furnace maintained at a temperature well above the melting point of copper. It was claimed that the oil base reduced the copper oxide present and also prevented oxidation of the copper which melted on the surface of the sheet. Although the method has been tried on a commercial scale, apparently with pronounced success, such sheets are not regular commercial materials.

The process is an adaptation of the earlier Siemens process used for the "coppering" of carbon brushes for electric generators and motors. In the Siemens process, the copper film is formed on the surface of the carbon by packing the brushes in finely divided copper mill scale (oxide) and heating to a temperature of approximately 400° C. The reduction of the oxide to metallic form gives a very adherent thin film of copper on the surface of the carbon. A process carried out in a manner quite similar to the Richards process is also utilized in ceramic work.

[22] Whitney, L. C., "Am. Soc. Metals Handbook," 1938.

[23] Richards, J. W., *Trans. Am. Inst. Mining Met. Eng.,* **60**, 365 (1919).

[24] Palmer, W G., *Trans. Am. Electrochem. Soc.,* **51**, 445 (1927).

A method often employed for producing a copper finish on wire consists in immersion of the wire in a solution of copper sulfate. The precipitated spongy copper is rendered firmly adherent by drawing the wire through a die and reducing it in size very slightly. The coating thus formed is primarily for improving the appearance of the wire rather than for protecting it from corrosion. Finally, copper coatings are readily produced by metal spraying, sputtering and evaporation methods.

Corrosion Resistance of Copper Coatings

As previously stated in this chapter the successful use of copper coatings for the protection of iron or steel is largely dependent upon the absence of pinholes or defects in the coating which expose the underlying metal. Electroplated copper coatings in the range ordinarily deposited are porous. This does not impair the usefulness of such deposits as undercoatings for nickel and nickel-chromium finishes and they are extensively used for such purposes. Sputtered coatings may be obtained which are non-porous; and, of course, mechanically applied copper coatings (*i.e.*, "copper clad" or "copper-welded") also fall in this category.

Electroplated copper coatings were formerly employed to a limited extent on apparatus parts used indoors and in protected locations where the appearance of the article was of no importance. In air at low relative humidities, copper readily tarnishes, the weight gain with time showing a parabolic relationship. At higher humidities pinhole rusting occurs on electroplated coatings on steel. In the case of pore-free coatings the unattractive tarnish film in outdoor exposures is succeeded in time by the development of the green patina characteristic of copper in such atmospheres. Studies [25] of this coating have shown that its main constituent is usually basic copper sulfate, $CuSO_4 \cdot 3Cu(OH)_2$, although near the sea it may contain varying amounts of basic chloride. Basic copper carbonate is present always in minor proportions. It has been claimed [26] that the protective agent in the patina is cuprous oxide under all circumstances. A synthetic patina may be produced on copper by anodic oxidation in a suitable electrolyte.[27]

Steel clad with copper by the mechanical process is employed for ground rods and anchor rods, in which case direct contact with soils is involved. Limited tests [28] made on rods of this type buried in three soils have shown results similar to those obtained for copper. In an acid muck (where the oxygen concentration is low) the copper-coated rods were but slightly attacked. This is in accordance with general experience with copper in acidic environments in the absence of oxygen. For example, recent studies[29] have shown that the rate of corrosion of copper in sulfuric acid is directly proportional to the solubility of oxygen up to a concentration of $25N$, beyond which the oxidizing character of the acid influences the rate. Incidentally, the presence of nitrates or other oxidants in the soil is known to cause marked corrosion of copper. In an arid, highly alkaline soil the rate of corrosion of the copper coatings was less than half that of bare ferrous specimens in the same soil. The attack was, however, characterized by pitting, which after four years extended through the coating in one instance. The most severely corrosive soil for the copper-clad specimens (although the coatings were still intact) was a salt marsh on the New Jersey coast. Similar results were obtained for copper pipe in the soil burial test conducted by the National Bureau of Standards.[30] Copper pipes buried at this location showed an average loss of weight of 0.57 ounce per square foot per year in this soil as contrasted with an average of 0.067 ounce per square foot per year in the other 33 soils employed in this test. The corrosiveness of tidal marshes toward copper is not due to sodium chloride but to sulfides apparently resulting from the bacterial reduction (by *Spirillum desulfricans*) of sulfates.[31] The corrosion product is copper sulfide which, upon attaining an appreciable thickness, may be scaled off in slabs. The odor of hydrogen sulfide is readily detected upon spading up the soil at this location and in other similar marshes.

---

[25] Vernon, W. H. J., and Whitby, L., *J. Inst. Met.*, 42, 181 (1929); 44, 389 (1930). Also, Freeman, J. R., and Kirby, P. H., *Metals and Alloys*, 3, 190 (1932); Vernon, W. H. J., *J. Chem. Soc.*, p. 1853 (1934).

[26] Haase, L. W., *Z. Metallkunde*, 26, 185 (1934).

[27] Vernon, W. H. J., *J. Inst. Metals*, 49, 153 (1932).

[28] Unpublished results reported by R. M. Burns and C. L. Hippensteel to the National Bureau of Standards Corrosion Conference in Washington, D. C., 1930.

LEAD COATINGS

Lead has many desirable features as a coating metal. Lead-coated sheet may be very seriously deformed without having the coating stripped off; hence such material finds considerable application in deep-stamping operations in which the coating aids materially by acting as a lubricant. The paint-holding properties of lead coatings are excellent. Lead is the only common coating metal which is resistant to sulfuric and sulfurous acid fumes.

Coatings of lead or lead-rich alloys are deposited by the hot-dipping process, by electroplating, and by the metal-spray process. Of greater importance, particularly in the chemical industry, are what is known as homogeneous lead linings which are applied to a great variety of equipment such as storage tanks, drums, autoclaves, pipes, agitators, propellers and mixing devices of all descriptions.[32] These coatings usually have a minimum thickness of $\frac{3}{16}$ inch.

The Hot-Dipping Process

When an iron or steel article is immersed in a bath of molten lead, no alloying occurs between the two metals even though the surface may have been thoroughly cleaned before immersion. The molten lead, therefore, does not readily "wet" the surface as zinc and tin do, and instead of forming a thin surface film over the immersed article, the lead coalesces more or less into drops and rivulets when the article is withdrawn from the lead bath. The same is true of brass and copper articles immersed in molten lead. Although lead coatings can be produced on iron and steel if great care is taken in cleaning the surface before attempting the hot-dipping process, such coated articles are always more or less unsatisfactory on account of the pronounced discontinuities that exist in the coating. The claim has been made [33] that if clean steel is dipped in a fluxing bath, consisting of a saturated solution of zinc chloride containing 5 per cent ammonium chloride, immediately before immersion in the molten lead (at 340 to 360° C.), a quite uniform coating of lead can be produced. Usually it is necessary to give the article two dips both in the flux and the lead bath.

---

[29] Damon, G. H., and Cross, R. C., *Ind. Eng. Chem.*, 28, 231 (1936).

[30] Logan, K. H., *Bur. Standards J. Res.*, 7, 585 (1931).

[31] von Wolzogen Kühr, C. A. H., *Water en Gas*, 26, 277 (1923); von Wolzogen Kühr, C. A. H., and van der Vlugt, *Water*, 16, 147 (1934); Bunker, H. J., *Corrosion Committee of Iron and Steel Inst. Fifth Report*, Sec. F(3), page 431 (1938).

[32] Mantius, E., and Freiherr, H. F., *Ind. Eng. Chem.*, 29, 373 (1937).

In order to form a "bond" for a lead coating, it has been the practice in the past to make use of some alloying element common to the two metals, lead and iron. Tin has been used for this purpose for many years as it alloys readily with both metals. Antimony may be used [34] and cadmium [35] and mercury [36] have also been tried with some success. Arsenic has also been recommended.[33]

The alloying element may be added in a considerable amount to the lead bath as is the case in the manufacture of terne-plate described below; or a film of the alloying element may be precipitated on the surface of the article to be coated by immersion in a suitable solution prior to passing through the molten metal bath. Electroplating with a suitable bonding metal before dipping in order to form the desired bonding film has also been used to a limited extent.

Lead coatings show a rather pronounced tendency toward formation of pinhole perforations as the coating solidifies. In the case of sheets such perforations can be removed by rolling the sheet after it has been coated. On articles of irregular shape, however, this cannot be done.

A process has been described [34] for the production of coatings of relatively pure lead on iron and steel. The material, after pickling, is immersed in a solution of antimony chloride; the film of precipitated antimony, by its alloying action after immersion in the bath of molten metal, serves as a binder for the coating. The molten metal bath used may be either commercially pure lead or an alloy of lead and antimony.

Antimony alloys very readily with lead. The two form a simple eutectiferous series, the eutectic containing 13 per cent antimony and melting at 247° C. The limit of solubility of antimony in solid lead has been shown[37] to be as low as 0.5 per cent at room temperatures increasing to 2.45 per cent at the eutectic temperature. Antimony also alloys readily with iron forming two compounds, Fe_3Sb_2 and Fe_2Sb_2, which have been reported in this alloy system.

---

[33] Maass, E., *Korr. Metallschutz*, **1**, 76 (1925), *Met. Ind. (London)*, **27**, 557 (1925). Also Westerkamp, H., *Chem. Ztg.*, **49**, 1056 (1925).

[34] Baskerville, Chas., *J. Ind. Eng. Chem.*, **12**, 152 (1920); U. S. Patent 1,378,439 (1921).

[35] Beneker, J. C., *Am. Gas Light J.*, **103**, 292 (1915); U. S. Patent 1,144,523, (June 29, 1915).

[36] *Iron Age*, **89**, 644 (1912); *Met. Chem. Eng.*, **10**, 253 (1912). Also, *Iron Age*, **99**, 1483 (1917).

A somewhat similar process, in which the articles to be coated were passed through a solution of mercuric chloride, has been tried on a commercial scale. The film of precipitated mercury served as the basis of the alloy-binding layer. On account of the dangers attending the use of the poisonous mercury solution, however, the process did not prove a commercial success.[36]

Some excellent "lead-coated" sheets have been made by using galvanized stock as a base upon which the lead coating was formed by immersion in molten lead. Commercial tin plate can be used in the same way as a base for subsequently coating with lead. A recent investigation[39] of lead-dipped coatings applied over zinc-plated steel has shown that a smooth, adherent, continuous coating of lead may be obtained within narrow limits of bath temperature, provided the molten lead contains a fractional percentage of zinc. The binding agent in this case appears to be needle-like crystals of zinc which extend into the lead layer and attach themselves through a solid solution of zinc in lead.

Lead Linings

A substantial veneer of lead on iron or steel, producing a duplex metal structure, is known as a lead lining, and is to be distinguished from the thinner coatings or coverings of lead obtained by hot dipping or electroplating. For many years, more or less loose linings of lead sheet have been used in supporting vessels of wood, brick or steel. In other instances such linings or coverings have been fastened or bonded at certain points.

In the early development of homogeneous lead linings, tin or solder was used to bond the lead layer to the steel. In recent years it has been possible to attain this end by the use of non-metallic fluxes, usually of secret nature. The steel surface is first cleaned thoroughly and pickled or sandblasted, before application of the flux. There are two general methods of application of the lead layer; molten lead may be poured on the fluxed surface or it may be "burned" or welded on by applying an oxy-hydrogen flame to bar lead.[40] In the latter case a thin skin of lead is first applied by a hot-dipping process, and in the subsequent building-up of the coating, each burned layer is cooled and scraped to remove traces of extraneous materials. The thickness of such a layer after scraping is

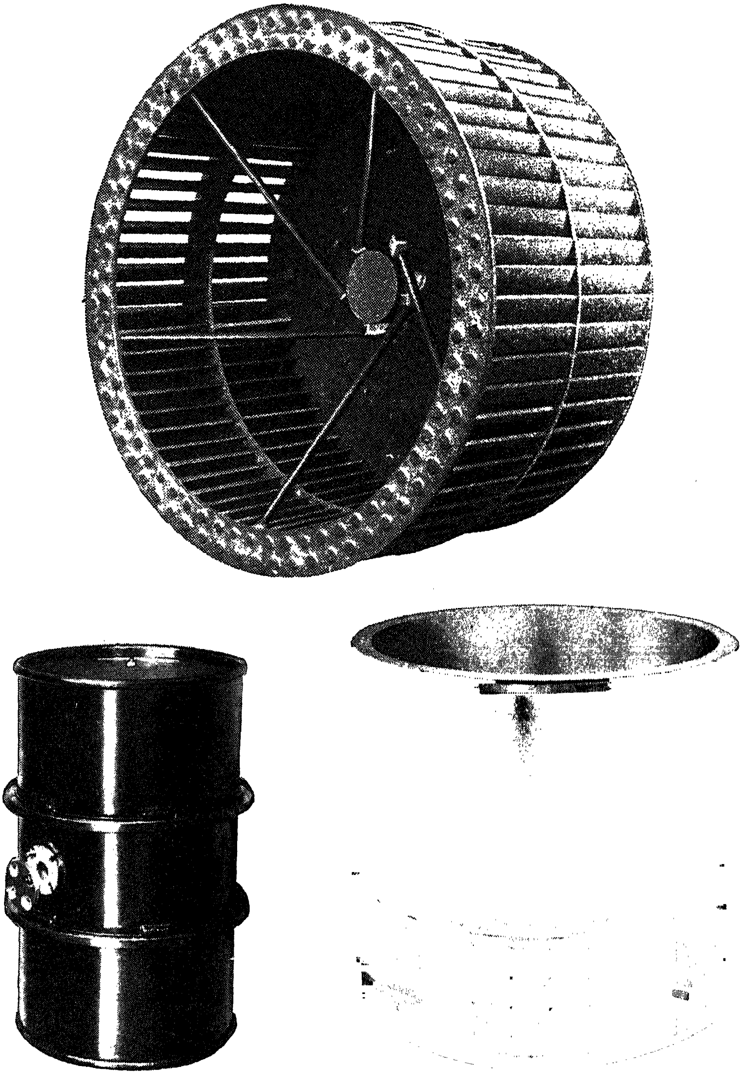
---

[37] Dean, R. S., Zickrick, L., and Nix, F. C., *Trans. Am. Inst. Mining Met. Eng.*, 73, 505 (1926).

[38] Kurnakow, N. S., and Konstantinow, N., *Z. anorg. Chem.*, 58, 1 (1908).

[39] Bray, J. L., *Trans. Am. Inst. Min. Eng. Inst. Metals Div.*, 124, 199 (1937).

[40] Schlundt, L. R., (Republic Lead Equipment Co.), Cleveland, O. *Private Communication*, July 25, 1938.



Courtesy of Republic Lead Equipment Co.

Figure 50.—Examples of Lead-Coated and Lead-Lined Equipment.

about $\frac{1}{16}$ inch and hence it requires four layers to obtain a coating $\frac{1}{4}$ inch in thickness. In Figure 50, examples of the types of equipment which may be readily lined or covered with homogeneous lead coatings are shown. Chemical lead is generally employed for linings of this sort, although lead hardened with antimony may be used for coatings of the loose type mentioned in the previous paragraph.

Terne-Plate

This material, often known commercially as "roofing tin," is not infrequently confused with true tin coatings. The name "terne," meaning dull, was originally used in contradistinction to "bright tin," that is, tin-plate. The composition of terne coatings varies within rather wide limits. Commercial terne coatings with a tin content as low as 12 per cent are made, as well as some containing as much as 50 per cent. The one most commonly used in this country, however, is a mixture of 75 per cent lead and 25 per cent tin.

Tin alloys readily with both lead and iron, and hence fulfills the condition necessary for a binder for a lead coating on iron. With lead, tin forms a simple eutectiferous series of alloys; the eutectic contains 63 per cent of tin[41] and melts at 182° C. The solid solubility of tin in lead is much less than formerly supposed; it varies from 2 per cent at room temperature to 18 per cent (approximately) at 150° C.[42] The alloying of tin and iron has previously been discussed.

The manufacture of terne-plate follows quite closely that of tin plate. Much of the light-coated product is made by means of a machine identical in all essential respects with that used for tin-plate of coke grade, the flux used being zinc chloride. The speed at which the sheets are passed through must be reduced in order to obtain as thick a coating as possible, and a higher temperature is required to maintain the bath in a molten state. In order to obtain a coating heavier than 15 pounds per base box, redipping of the sheets after they have passed through this machine is necessary.

A great deal of terne-plate, however, is still made by a process quite similar to the hand-dipping process originally used for tin plate. The essentials of the process are as follows:[43] After the final pickling the clean sheet is kept under water until ready to be immersed in a bath of hot palm oil. After a period of about 20 minutes in the oil, it is immersed in a bath of molten "terne" alloy which is kept covered with an oil layer. From here the sheet is passed into a second pot of molten metal and kept for several minutes. Upon removal from the second pot, the sheets are examined and cleaned, if necessary, before they are dipped into a third pot of metal, this one being of the highest purity of the three used. The sheets are then transferred with as little delay as possible to a bath of hot palm oil where they are allowed to "sweat," the sweating period being determined by the weight of coating desired. If left too long in the hot oil, the coating may be entirely sweated off. The sheets are finally cleaned, as in tin-plate manufacture, in a branding machine. They are finished with either an oil or dry finish. A terne coating, on account of the lead contained, does not have the bright finish of tin plate, no matter how much it may be polished.

[41] Rosenhain, W., and Tucker, P. A., *Phil. Trans. Roy. Soc.*, **209 A**, 89 (1908).

[42] Paravano, N., and Scortecci, A., *Gazz. Chim. Italiana*, **50**, pt. 1, 83 (1920).

[43] Camp, J. M., and Francis, C. B., "The Making, Shaping and Treating of Steel," 4th ed., pp. 1016-1023, Carnegie Steel Co., Pittsburgh, Pa. (1925).

During the solidification of the coating, a characteristic surface network or crystal pattern is formed which is analogous to the spangle on zinc-coated sheet. This appearance is known as "mottle" and the size of the network increases with the thickness of the coating. It serves a rather useful purpose, therefore, as an index of the weight of coating.

The finished sheets are carefully inspected and graded. Since a great part of commercial terne-plate is used for roofing and similar purposes for which it is usually necessary to use the entire sheet, without cutting it, very close inspection and grading are necessary. The "prime" sheets must be free from all visible defects and even in the "menders" only such defects as can be remedied by redipping the sheet are permitted. The sheets of the "stripper" grade correspond to the seconds in tin-plate. They may be rerun and converted into primes having a lighter-weight coating. The sheets of "scrap" grade are of no practical use.

The weight of coating on terne-plate is expressed in a manner similar to that used for tin-plate. In this case, the base box consists of 112 sheets, 20 by 28 inches. The weight of coating varies according to the grade, from 8 to 40 pounds per base box. One pound per base box is approximately equivalent to 0.00002 in. The following weights of coating have been generally agreed upon by manufacturers, distributors and users:[44] 8, 15, 20, 25, 30, 32, and 40 pounds per base box; the two weights, 12 and 35 pounds per base box, formerly used, have been discontinued.

Most of the sheets used for making terne-plate for roofing purposes are either of the IC weight, approximately 30 U. S. standard gauge, or IX which is approximately 28 gauge in thickness. In the agreement mentioned above it was recommended that no terne-plate lighter than IC in thickness henceforth be manufactured for roofing purposes in 28- by 20-inch sheets, commonly termed "short ternes."

The use of terne-plate for other uses than roofing has recently increased greatly. The material is admirable for deep stamping operations and nearly 40 per cent of the amount manufactured now is used in this manner.[43] Large quantities are used in the manufacture of gasoline tanks. Sheets much larger and heavier than the roofing size are manufactured for such purposes. They are known as "long ternes" by the trade.

Coatings of lead or of lead-rich alloys afford only a mechanical protection of iron against corrosion. Terne-plate of the heavier weights of coating, for example, 25- to 40-pound coatings, however, gives very satisfactory service as roofing material. It is necessary that such roofs be kept painted. Benches and cabinets for chemical laboratories are often fabricated from terne-plates or lead-coated steel and finished with an acid-resistant paint. The excellent paint-holding properties of such coatings compensate for some of the possible shortcomings which might be expected of coatings of this kind. The resistance of lead coatings to corrosive attack by sulfuric acid also makes them valuable for service for which coatings such as zinc are entirely unsuited.

---

[44] "Simplified practice recommendation No. 30. Terne-plate," U. S. Bur. Standards, Washington, D. C. (1925).

Electroplated Lead Coatings

The commercial application of lead plating is quite limited. Most of the practical applications of this type of protective coating depend upon the resistance of lead to attack by sulfuric acid. The usefulness of such coatings for protecting steel against an attack of this kind as well as from some of the special chemicals developed for chemical warfare was strongly emphasized by experience during the war,[45] although very considerable study of lead plating had been done before that time.[46]

Lead can be electrolytically deposited rather easily from a number of solutions but, largely on account of its tendency to form "trees" when deposited from certain solutions, the baths used commercially are limited to three [4] which are rather complex in their composition: the fluosilicate, the fluoborate, and the perchlorate solutions of lead. An addition of some substance such as glue is practically always necessary in order to ensure a dense impervious coating. The fluosilicate bath [47] is composed of lead fluosilicate ($PbSiF_6$) and "free" fluosilicic acid in varying proportions to give a fluosilicate radical concentration of about $2N$. The range of "free" acid used is from 0.25 to $1.2N$. The fluoborate solution [48] is prepared by mixing hydrofluoric and boric acids and then adding basic lead carbonate to the mixture. Satisfactory thick deposits may be obtained from plating solutions in which the lead content is $2N$ and the total fluoboric acid $3N$, operating at a current density of 3 amperes per square decimeter (28 amp./sq. ft.). The perchlorate bath [46] consists of basic lead carbonate dissolved in perchloric acid. The range of concentration usually employed is about 0.4 to $0.6N$ in lead and 0.2 to $0.4N$ in free acid. Alloys of lead and tin may be electrodeposited from fluoborate solutions [49] and have been used for the inside of air-flasks for naval torpedoes.

Corrosion Resistance of Lead Coatings

Porous or very thin lead coatings do not provide satisfactory protection to steel in acidic and neutral environments owing to the development of pinhole rusting. This action is less pronounced and may not occur under mildly alkaline conditions. The thickness of coating required to insure continuity and freedom from pores or bare spots depends upon the coating process employed, plated coatings being the most dense and sprayed coatings the most porous. Hot-dipped coatings are generally not free from pores. Slightly porous coatings may be improved very materially by slightly working or burnishing the surface. Lead linings which are usually at least 0.25 inch are of course non-porous.

---

[45] Mathers, F. C., *Metal Ind. (N. Y.)*, 13, 184 (1915); Reeve, A. G., *Trans. Am. Electrochem. Soc.*, 35, 389 (1919).

[46] Mathers, F. C., *Trans. Am. Electrochem. Soc.*, 23, 153 (1913).

[47] Betts, A. G., "Lead Refining by Electrolysis," New York, John Wiley & Sons, 1908.

[48] Blum, W., Liscomb, F. J., Jencks, Z., and Bailey, W. E., *Trans. Am. Electrochem. Soc.*, 36, 243 (1919).

[49] Blum, W., and Haring, H. E., *Trans. Am. Electrochem. Soc.*, 40, 287 (1921).

Electroplated lead coatings 0.004 inch in thickness have been found to give excellent protection to iron and steel exposed to the atmosphere.[50] It seems likely that a thickness of 0.003 inch will usually be pore-free and therefore adequate for ordinary outdoor service. For chemical equipment plated coatings 0.05 inch or greater [51] in thickness are desirable.

Sprayed coatings of lead are readily applied, and as is the case for other metals applied by spraying it is customary to use relatively thick coatings of lead. It has been recommended [52] that coating thicknesses of 0.2 millimeter (0.0078 inch) be employed for prevention of the rusting of steel in the atmosphere, 0.3 to 0.4 millimeter (0.012 to 0.016 inch) for resistance to sea-water and not less than 2.0 millimeters (0.078 inch) for dilute sulfuric acid. Usually lead linings of substantially greater thickness are used in the chemical and petroleum industries.

Lead coatings which are substantially pore-free are resistant to corrosion in the atmosphere because of the formation of a superficial oxide film, relatively impervious in character, which may preserve the metal and therefore protect the underlying ferrous base for long periods of time. Upon injury to the coating, this protective film repairs itself. Usually lead-coated materials will stand severe deformation without noticeable damage to the protective quality of the coatings. The softness of the metal does impose some limitation, however, on the use of lead coatings on hardware and other articles subject to considerable mechanical abuse.

The corrosion resistance of lead to many chemicals, such as sulfuric and hydrochloric acids, brines, etc., has given rise to the use of heavy lead linings in tanks, pipes, pumps and other equipment used in the manufacture and storage of such products. One of the most important single commercial applications of lead plating is for the fittings of storage batteries. Lead plating has also been recommended [48] for lining the copper shells of the ordinary hand fire-extinguisher and for lining flues for conducting the waste gases from gas heaters. In lead-lined fire-extinguishers it has been found [53] that the addition of one ounce of sodium phosphate per gallon of water inhibits the corrosion of both the lead coating and any exposed areas of steel; sodium silicate has been found effective for the same purpose.

The use of lead for water pipes, at one time quite extensive, and the fact that this metal is generally corroded less rapidly by soils than iron and steel, have led to the consideration of lead coatings for pipes used underground. Accordingly, lead-coated pipe specimens were included in the soil corrosion test started by the National Bureau of Standards in 1922. Specimens of steel pipe 6 inches in length and 1.5 inches in diameter with hot-dipped lead coatings of about 0.001 inch in thickness were buried in

---

[50] Kurrein, H., *Werkstattstechnik,* **26,** 458 (1932).

[51] Krause, H., *Feinmechanik Präzison,* **40,** 106 (1932).

[52] Forstner, H. M., *Oberflachentechnik,* **11,** 173 (1934).

[53] Hewlett, *J. Soc. Chem. Ind.,* **54,** 1094 (1935).

47 soils of diverse character. Actual measurements of coating thickness showed that there was considerable variation in thickness over the pipe. The results obtained at the end of approximately ten years are given in Table 25[54] which includes for comparison the corrosion rates obtained for steel pipes of the same dimensions and specimens of lead cable sheath-

Table 25.—Corrosion of 1½- by 6-inch Lead-coated Pipe Exposed for Approximately 10 Years.

		Rates of loss (oz./ft.^{2}/yr)			Rates of maximum penetration (mils/yr)		
Soil	Soil type	Lead-coated steel	Bare steel [1]	Lead cable sheath [1]	Lead-coated steel	Bare steel	Lead cable sheath
1	Allis silt loam	0.529	0.80	0.173	11.9	5.8	8.1
2	Bell clay	.102	.49	.067	4.0	6.7	1.8
3	Cecil clay loam	.066	.43	.059	3.6	4.5	1.4
4	Chester loam	.239	.52	.177	7.0	6.8	4.0
5	Dublin clay adobe	.597	.45	.135	6.9	3.1	3.8
6	Everett gravelly, sandy loam	.096	.08	.025	2.0	1.4	0.8
7	Unidentified silt loam	.207	.37	....	7.0	2.5	...
9	Genesee silt loam	.080	.43	....	5.0	4.5	...
10	Gloucester sandy loam	.163	.36	.088	6.5	3.2	1.2
11	Hagerstown loam	.071	.16	.034	3.4	4.9	1.2
13	Hanford very fine sandy loam	.064	....	....	5.4	...	...
14	Hempstead silt loam	.036	.39	.049	4.2	7.1	1.7
15	Houston black clay	.052	.65	.036	3.2	4.4	2.2
17	Keyport loam	.379	.77	.028	4.7	3.3	1.7
18	Knox silt loam	.046	.23	.016	4.6	3.2	1.1
20	Mahoning silt loam	.224	.52	.268	5.3	5.5	4.1
22	Memphis silt loam	.192	.61	.085	7.3	6.6	1.2
24	Merrimac gravelly, sandy loam	.033	.12	.015	2.2	2.1	1.5
27	Miller clay	.231	.63	.067	5.6	4.9	2.4
28	Montezuma clay adobe	.314	1.75	.069	7.8	15.1	0.9
29	Muck	.689	1.61	.343	6.3	12.0	.9
31	Norfolk sand	.028	.22	.022	1.5	2.5	.5
32	Ontario loam	.072	.32	.028	5.2	4.3	1.5
33	Peat	.537	1.22	....	7.7	8.9	...
35	Ramona loam	.011	.09	.017	(2)	0.4	2.3
36	Ruston sandy loam	.032	.24	.032	1.8	3.9	1.1
37	St. Johns fine sand	.202	.58	....	6.4	5.6	...
38	Sassafras gravelly, sandy loam	.053	.22	.025	3.4	2.5	1.7
40	Sharkey clay	.191	.56	....	6.2	6.6	...
41	Summit silt loam	.051	.45	.039	5.8	7.6	1.5
42	Susquehanna clay	.092	.95	....	4.6	7.1	...
43	Tidal marsh	.726	1.47	.019	18.8	8.7	1.0
45	Unidentified alkali soil	.198	.79	.021	9.2	6.9	1.7
46	Unidentified sandy loam	.033	.37	.015	4.5	8.8	1.0
47	Unidentified silt loam	.184	.23	.122	6.1	2.4	5.7

[1] Bessemer steel pipe 1½ by 6 inches and commercial lead cable sheath in sheets 20¾ by 3½ by 0.112 inch removed from sites at the same time the lead-coated specimens were removed, were buried, in most cases, 1 or 2 years longer. The figures given are the averages from 2 specimens in the case of the steel and 1 specimen in the case of the lead sheath. The penetration of the sheath was determined by averaging 2 pits, each of which was the deepest on one side of the specimen. These pits were, of course, somewhat deeper than would be expected on specimens of the same exposed area as that of the pipe.

[2] No pits.

---

[54] Logan, K. H., and Ewing, S. P., *Nat. Bur. of Standards J. Research,* 18, 361 (1937).

ing (approximately 21 by 3.5 by 0.1 inches in size) buried in the same soils. The figures given in the table are the averages of two specimens, except in the case of cable sheath of which one specimen was used.

It will be observed that severe pitting of lead-coated specimens occurred in several soils in which the attack on commercial lead cable sheath was very mild. The generally greater rate of corrosion of lead coatings as compared with lead sheath suggests that the porosity of the coating may accelerate attack in soils much as it does in many other environments. The weight losses are seen to be greater in all instances for bare steel than for the lead-coated specimens, although this is not true for pit-depth. In a later comparative test [54] of lead-coated and bare steel specimens conducted by the Bureau of Standards for a period of only 2 years, it was found that the coating reduces corrosion in the early stages, but that after the coating becomes penetrated the rate of penetration of the steel is often accelerated. From a knowledge of the character of the soils used in these tests it has been deduced that lead coatings show up to the best advantage and are of some value in reducing corrosion in soils which are well drained and of high resistivity. Incidentally the coatings of two different manufacturers were similar in behavior in these soil tests.

Evidently the character of the soil is of considerable importance in determining the corrodibility of lead coatings. It has been shown in other studies[55] that the nature of the soil is more influential on the rate of corrosion than is the composition of the lead alloy.

The mechanism of corrosion in soils is a complex matter. The physical structure of soils, the size and adsorptive capacity of soil particles, permeability to air and moisture, the oxygen and carbon dioxide content of soil air, and the chemical composition of soluble acids and bases present in the soil are variables which must be taken into consideration in soil corrosion reactions. Much of the corrosion of lead, and presumably of lead coatings, which takes place in soils would seem to occur by means of the operation of differential aeration cells produced by contact of the metal surface with soil particles and aggregates. Studies [56] of lead specimens buried in pure sands have shown that relatively large particles are the most effective in producing differential aeration, and that on the other hand particles of colloidal size may even provide protection against corrosion. It will be borne in mind that the occurrence and nature of the corrosive action depends largely upon the effect of the constituents of the environment upon the operation of the corrosion cells. That is, the metal, as explained in Chapter 1, may either corrode or develop a more or less protective film, depending upon whether corroding or protective constituents are preponderant. In the case of lead in soils, the principal corroding elements are oxygen, nitrates, chlorides, alkalies and organic acids and the principal protective agents, silicates, sulfates, carbonates, colloidal substances and certain organic compounds.[55] Usually soils contain varying proportions of most of these substances and consequently the character of corrosion may depend upon the ratio of the concentrations of corroding to protective constituents.

---

[55] Burns, R. M., *Bell Sys. Tech. J.*, 15, 603 (1936).

[56] Burns, R. M., and Salley, D. J., *Ind. Eng. Chem.*, 22, 293 (1931).

Finally, to return to the question of the practical value of lead coatings for the protection of iron and steel underground, it is evident from the results given in Table 25 that in certain soils lead coatings are of definite advantage. However, the results of this test scarcely encourage the general use of lead coatings for protection against soil corrosion.

Aluminum Coatings

Aluminum is used as a protective coating for iron and steel and for alloys of aluminum, such as Duralumin, which in ordinary environments are susceptible to corrosion. An important application of aluminum is in the prevention of oxidation of ferrous metals at elevated temperatures. As judged from its markedly electronegative potential, aluminum coatings would be expected to provide cathodic protection to iron at pores or other flaws in the coating which expose the underlying metal. However, owing to the fact that aluminum reacts avidly with oxygen, a superficial oxide film, which is relatively inert and confers an apparent nobility upon the metal, is formed in ordinary environments. In consequence, aluminum offers little if any electrochemical protection to ferrous metals except in chloride solutions; its virtue as a protective metal lies principally in the inherent corrosion resistance of the oxide film which forms on its surface. A further and marked increase in the protective quality of the surface film on aluminum is obtained by anodic oxidation of the metal in a suitable solution, and this process is described in greater detail in Chapter 16.

Coatings of aluminum may be applied by hot-dipping, by cementation, by metal spraying and by mechanical methods. Aluminum may be electrodeposited successfully from non-aqueous solutions,[57] but the process has not as yet attained commercial importance.

Hot-Dipped Aluminum Coatings

Aluminum alloys very readily with iron; hence the fundamental condition for successful coating by hot-dipping is fulfilled. Iron and aluminum are completely miscible in the molten state. In aluminum-rich mixtures, the iron precipitates from the solution, upon solidification of the eutectic (655° C.) as the compound $FeAl_3$ (41 per cent iron). The solubility of iron in solid solution in aluminum is almost nil. Aluminum-rich alloys of the series, up to 41 per cent of iron, have a structure consisting of a matrix which is essentially pure aluminum, embedded in which is a hard, brittle constituent, the compound $FeAl_3$. On the other hand, aluminum is readily soluble in iron, as much as 35 per cent of aluminum being retained in solid solution in α-iron.[58]

Success in the hot-dipping of iron in aluminum is attained with difficulty and only after special preparation of the surface of the iron. Much of the difficulty is to be attributed to the tenacious film of aluminum oxide which forms so readily, and goes to the iron-aluminum interface in the dipping operation. Another factor of importance is the large amount of iron-aluminum compound which forms. This compound ($FeAl_3$) is brittle and should not exceed 0.01 mm. (0.00039 inch) in thickness if the coating is to possess satisfactory mechanical properties.[59] The thickness of the layer increases more rapidly with increasing bath temperature than with increasing time of immersion.[60] In preparing the iron surface for hot-dipping it is essential that all oxide (which interferes with diffusion) be removed; and one method of accomplishing this result is by immersion in molten salt mixtures. Many other methods have been proposed for overcoming the obstacles inherent in the process. For example, a thin layer of cadmium may be deposited on the iron surface and the part preheated before immersion in molten aluminum.[61] Presumably in this case the cadmium vaporizes permitting access of molten aluminum to the clean iron surface in the absence of air. In a somewhat similar process [62] tin- or zinc-coated steel is passed into molten aluminum and the previously coated surfaces mechanically abraded during immersion. Steel strip has been coated with aluminum by first fluxing in zinc-ammonium chloride, and then passing the strip through molten lead into the aluminum bath, the fluxing and dipping operation both being carried out in a reducing atmosphere.[63] In the process most recently developed [64] steel wire or sheet is degreased and pickled in an alkali or acid solution, then heated to about 600° C., fluxed by passing through a concentrated solution of boric acid or borax, heated in hydrogen at a temperature in excess of 732° C. (usually 900-1000° C.) and then passed into the molten aluminum bath which is maintained in a hydrogen atmosphere. Finally, the sheet is wiped. The increased hydrogen absorption in the higher temperature range is said to decarburize the steel surface and saturate it with hydrogen. In coating wire by this process at speeds of 10 to 50 feet per minute, the thickness of the $FeAl_3$ layer does not exceed 2 or 3 ten-thousandths of an inch. It is understood that this process is in successful commercial use.

---

[57] Blue, R. D., and Mathers, F. C., *Trans. Electrochem. Soc.*, **69**, 529 (1936).

[58] Kurnakow, N., Urasow, G., and Grigorjew, A., *Z. anorg. Chem.*, **125**, 207 (1922).

Calorizing

Calorizing is the trade-name for the cementation of a metal surface by means of aluminum. The process was developed at the Research Laboratory of the General Electric Company [65] and is intended primarily as a means of protecting iron from oxidation at elevated temperatures rather than from the more familiar type of corrosion. Usually the depth of penetration of aluminum is from 0.005 to 0.04 inch, the iron-alloy layer containing about 25 to 35 per cent aluminum.

---

[59] Zeerleder, A. V., *Korr. Metallschutz*, 12, 275 (1936).

[60] Röhrig, H., *Z. Metallkunde*, 26, 87 (1934).

[61] Sutton, H., *Brass World*, 25, 287 (1929).

[62] Uyeno, S., German Patent 265,248 (May 24, 1912).

[63] Dellgren, K., German Patent 632,993 (June 5, 1936); French Patent 743,843 (April 7, 1933).

[64] Fink, C. G., U. S. Patent 2,082,622 (1937).

[65] Ruder, W. E., *Trans. Am. Electrochem. Soc.*, 27, 253 (1915).

The method is quite similar to that of sherardizing. The articles to be treated are packed in a drum in a mixture of powdered aluminum, aluminum oxide and a small proportion (from 1 to 5 per cent) of ammonium chloride. The drum is slowly rotated as it is being heated and an inert atmosphere, usually of hydrogen, is maintained within it. The aluminum content employed in the process may vary from 5 to 50 per cent according to the service to which the treated piece is to be put. For steel and iron a calorizing temperature of 850 to 950° C. has been recommended, and for copper and brass parts, 700 to 800° C. The rate of diffusion of aluminum into iron rises abruptly at the A_3 point (906° C.).[66] The purpose of the alumina is to prevent coalescence of the particles of aluminum, as the temperature used is very considerably above that of the melting point of aluminum (660.2° C, 1220° F.). The aluminum and the chloride must be renewed from time to time as the mixture is used.

The calorizing process may be carried out by using steel previously coated with aluminum by the hot-dipping method.[67] Upon heating, the aluminum diffuses into the underlying metal, producing a coating which is essentially the same as that obtained by the original calorizing method, although thinner and less protective.

In addition to utilizing the hot-dipping process as a part of the calorizing treatment, various other modifications have been proposed. For example, if iron is placed in an inert or reducing atmosphere containing dry aluminum chloride gas at a temperature of 750-1100° C., metallic aluminum is deposited, replacing the iron, atom by atom, according to the reaction:[68]

$$\underset{\text{Vapor}}{2AlCl_3} + \underset{\text{Solid}}{3Fe} \longrightarrow \underset{\text{Vapor}}{3FeCl_2} + \underset{\text{Solid}}{2Al}$$

The aluminum coating obtained by this process is essentially the same in appearance, structure and properties as that made in the regular calorizing process. It is possible to use illuminating gas, ammonia or ammonium chloride instead of hydrogen in this process.

Considerable advantage may be gained by spraying with aluminum, by the metal-spraying process, parts to be used at high temperatures, such as furnace grate bars and other furnace parts.[69] When heated in the presence of air, such coatings form a tough, adherent oxide layer; alloying with the base metal also occurs. It may be considered, therefore, that a calorized layer is produced. The life of such sprayed aluminum coatings is very much less than that of the regular calorized product, but likewise the initial cost and the cost of renewal are correspondingly less.

---

[66] Kase, T., Kinzoku no Kinkyu, **12**, 66 (1935).

[67] Howe, G. H., and Brophy, G. R., *Gen. Elec. Rev.*, **25**, 267 (1922).

[68] Martin, E. D., *Doctor's Thesis Univ. Nancy* (1924); *Cournot, J., Rev. Métal,* **22**, 139 (1925); "Metal Coating Processes," *Calibron Notebook No. 4* (1937), Calibron Products, Inc., West Orange, N. J.

[69] Hopfelt, R., *Z. Ver. deut. Ing.*, **69**, 411 (1925).

The aluminum deposited during calorizing alloys with the basis metal. The outer hard, rough, porous layer of the coating formed consists largely, in the case of iron, of the aluminum-rich compound, $FeAl_3$, and on account of its porosity affords little if any protection to the treated metal. Beneath the outer layer is a region which is considered to be a solid solution of aluminum in the basis metal. It is to this layer, the structure of which is shown in Figure 51, that the characteristic behavior of a calorized metal is to be attributed.

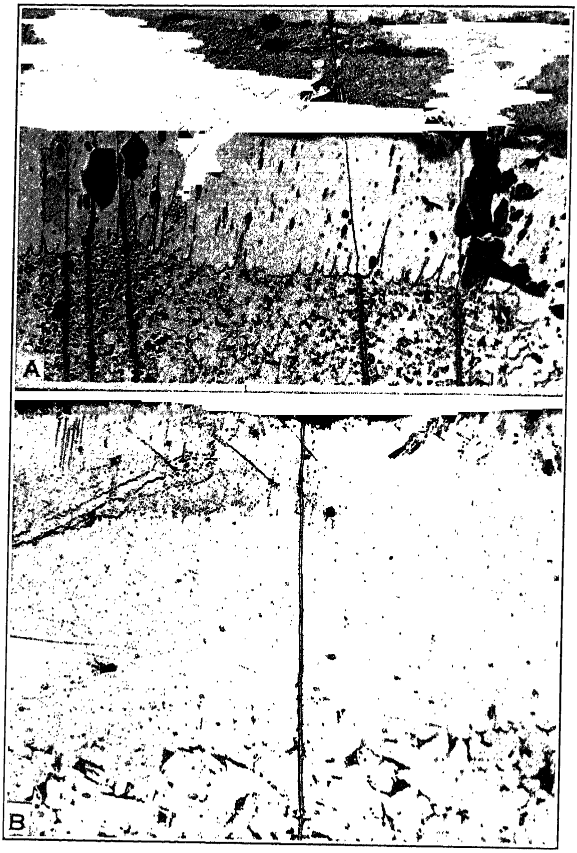


Figure 51.—Structure of an Aluminum Coating on Steel, ×100. Etchant, Alcoholic Solution of Nitric Acid.

A. The coating was formed by dipping in molten aluminum. It consists of two layers, the outer soft one of aluminum (upper part), and a hard alloy adjacent to the steel. The scratches were drawn for purpose of showing the relative hardness of the layers.

B. Coating on a steel rod "calorized" by the commercial powder method. The coating consists of a solid solution of aluminum in iron. By heating A, a coating similar to B would be produced.

The calorizing treatment is especially to be recommended as a protection against oxidation at high temperatures. In Figure 52[65] are given relative rates of oxidation of iron in the treated and untreated condition at 800 °C. and 1000° C. (1470 and 1830° F.), and it will be observed that calorizing exerts a marked retardation on the rate of gain in weight. The pronounced difference in scaling between calorized and untreated steel pipe, when subjected to high temperature for several hours, is shown in Figure 53.[70]

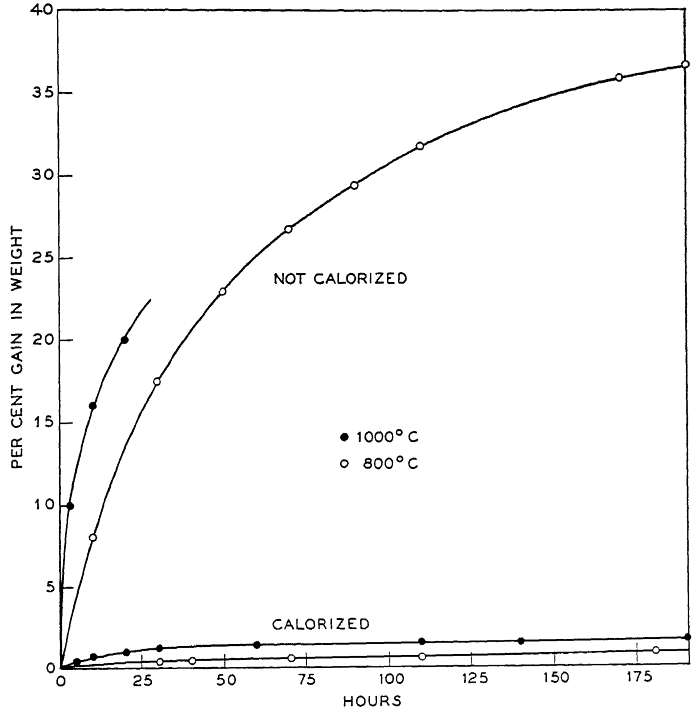


Figure 52.—Rate of Oxidation of Calorized and Uncalorized Iron.[65]

Most of the resistance to oxidation at high temperatures shown by calorized metal can be attributed to the tenacious coating of aluminum oxide which readily forms in the early stage of the heating and prevents further oxidation of the underlying metal. The calorized coating when first put on is quite thin, being only 0.001 to 0.004 inch in thickness. Upon heating, however, the aluminum diffuses deeper into the metal and the coating becomes thicker, but of necessity, has a lower average aluminum content. This factor is of importance as it limits the temperature at which calorized metals may be used to best advantage. If the outer protective layer of alumina becomes broken after the article has been used for a time it cannot be renewed as the aluminum content of the underlying layer has been lowered too much as a result of diffusion. Under these circumstances deterioration of the entire article may result in a short time.

---

[70] Allison, H. B. C., and Hawkins, L. A., *Gen. Elec. Rev.*, 17, 947 (1914).

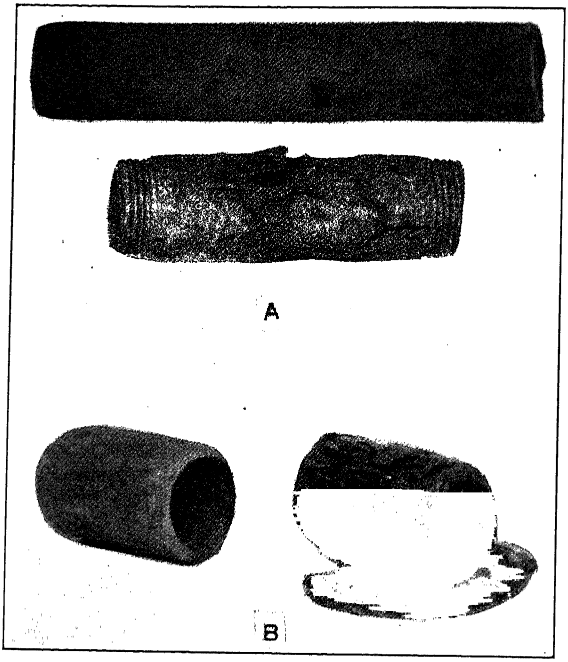


Figure 53.—Appearance of Calorized and Uncalorized Steel Pipe after Heating.[70]

A. 900° C. (1652° F.) 8 hours.
B. 800° C. (1472° F.) 100 hours.
The uncalorized pipe in each case shows pronounced scaling.

It has been estimated[71] that the life of calorized iron below 900° C. (1650° F.) should be almost unlimited; if it is used at 900 to 980° C. (1800° F.), the probable maximum life will be 20 times that of an untreated piece, while if the service temperature is 980 to 1100°C. (2010° F.), the life may be 5 times that of an untreated piece.

Calorized metals will not stand severe deformation without damage to the coating. On iron heavy calorized coatings are sufficiently tough to stand about 5 per cent elongation. Calorized iron is resistant to sulfurous gases and to fused salts at high temperatures, but is corroded by aqueous solutions of mineral acids.[72] Calorizing has found an important application in the oil-refining industry[73] in equipment, such as tube stills for cracking and topping, as well as valves, retorts, and condenser parts. In addition to its use for furnace parts, such as conveyors, stokers, roasters, rotary dryers, kiln parts, carburizing and heat-treatment boxes, and pyrometric equipment, important applications are being made[74] in Diesel engine construction, in the carbon and coke industry, as well as many relatively minor miscellaneous fields where resistance to oxidation and sulfur attack at high temperature is involved.

---

[71] Cournot, J., *Rev. Métal*, 23, 219 (1926); *Compt. rend.*, 182, 696 (1926).
[72] Sayles, B. G., "Am. Soc. Met. Handbook," 1938.

Mechanically Applied Aluminum Coatings: "Alclad" Products

Although sheet steel has been coated with aluminum by a mechanical or welding method the product has not been of commercial importance. On the other hand, the coating of aluminum alloys with commercially pure aluminum, or other aluminum alloys as mentioned in Chapter 3, has become an important method for protection of these alloys against corrosion. These products are designated by the American producer as "Alclad" alloys. They are made by casting an ingot of an alloy, such as Duralumin, in a steel mold lined with sheet aluminum or aluminum alloys.[75] Usually the mold is water-cooled or chilled to prevent excessive diffusion of the molten alloy into the aluminum. The aluminum-coated ingot produced in this manner is rolled to suitable dimensions without fracture of the coating, the initial ratio of the thicknesses of sheet metal and alloy being maintained.

"Alclad" aluminum alloys have found wide application in the aircraft industry and in other fields where it is essential that alloys of the Duralumin type be effectively protected against corrosion. In the construction of airplane fuselages it is common practice to employ an "Alclad" alloy in the form of sheet stock and formed supporting ribs. The shell of the all-metal dirigible ZMC-2 consists of "Alclad" 17S-T having a wall thickness of 0.0095 inch (0.24 mm.), and it has shown no loss in properties after more than five years' service.[76] It is of interest to note that the coating metal or alloy is so selected as to be anodic to the core alloy and in that way to furnish electrochemical protection to exposed edges or portions of the core material.

Corrosion Resistance of Aluminum Coatings

Atmospheric exposure tests of aluminum-iron couples conducted under the auspices of the American Society for Testing Materials in nine localities have indicated[77] that aluminum provides little if any electrochemical protection to bare iron at cracks or flaws in the coating. While there was evidence in this test of slight cathodic protection to iron in atmospheres high in chlorides (at La Jolla, California and Key West) there was practically no galvanic activity in rural and urban localities such as State College, Pa., and Rochester, N. Y., respectively. These results are consistent with observations [78] of the behavior of fractured sprayed aluminum coatings on steel exposed to a rather hard city water and to a $0.5N$ sodium chloride solution. In the first case the exposed iron surface rusted, but in the salt solution the adjacent aluminum coating cathodically protected the bare iron from corrosion. It would appear that destruction of the oxide film on aluminum by means of chlorides permits the aluminum-iron couple to function, corroding aluminum and protecting iron.

---

[73] Wilson, R. E., and Bahlke, W. H., *J. Ind. Eng. Chem.*, **17**, 355 (1925).

[74] Farr, A. V., *Iron Age*, **107**, 251 (1921).

[75] Dix, E. H., U. S. Patent 1,865,089 (1932).

[76] Frary, F. C., *Trans. Electrochem. Soc.*, **70**, 131 (1936).

[77] Hippensteel, C. L., "Symposium Outdoor Weathering of Metals and Metallic Coatings," *Am. Soc. Test. Mat.*, p. 99, (1934).

Sprayed aluminum coatings employed in industry are usually from 0.006 to 0.010 inch in thickness, and for severe exposures even 0.015 inch is recommended. Aluminum coatings applied by hot-dipping, like coatings of zinc and tin produced by this method, may be expected to be porous in thicknesses under 0.001 inch. On "Alclad" alloys the pure aluminum layer on thin sheet (0.010 inch) may be only 0.00055 inch in thickness, yet it possesses a high degree of continuity. It is of interest to note, as has been previously mentioned, that the exposed edges of the alloy layer of "Alclad" sheet do not corrode, owing to the fact that the coating is sufficiently anodic to the alloy to induce cathodic protection.[79]

Upon exposure to the atmosphere freshly abraded aluminum rapidly forms an impervious oxide film of the order of a millionth of a centimeter in thickness.[80] After the first few days of exposure the weight-increment curve becomes parallel with the time axis. That is, after 10 to 14 days, the primary film ceases to thicken. The self-healing and inert character of this film provides considerable resistance to ordinary atmospheric corrosion. After long periods of exposure, there is evidence of subsidiary increases in weight of aluminum test specimens which may be due to the repair by oxidation of fissures or cracks which have developed in the primary film. In any case, the rate of corrosion eventually attains a very low value.[81] It has been shown,[82] for example, that although aluminum wire lost approximately 12 per cent in tensile strength and 49 per cent in elongation in the first eight years of exposure to the London atmosphere there was no further loss in these properties in the succeeding 15 years. More recent tests [83] on Duralumin-type alloys have shown that corrosion is practically self-stopping within a few weeks or months depending upon the character of the exposure, and that the depth of penetration is independent of the thickness of the section. It is evident that aluminum coatings should be of sufficient thickness to take advantage of the self-stopping

---

[78] Evans, U. R., *J. Inst. Metals*, **40**, 99 (1928).

[79] Edwards, J. D., and Taylor, C. S., *Trans. Am. Electrochem. Soc.*, **56**, 27 (1929).

[80] Vernon, W. H. J., *Trans. Faraday Soc.*, **23**, 113, especially 150 (1927).

[81] Dix, E. H., *Proc. Am. Soc. Test. Mat.*, **33**, pt. 2, 405 (1933); see also discussion of same paper by Rawdon, H. S., and Mutchler, W. H., *ibid.*, 414.

[82] Wilson, E., *J. Inst. of Elec. Eng.*, **69**, 89 (1930).

[83] Dix, E. H., *Proc. Am. Soc. Testing Materials*, **33**, pt. 2, 405 (1933); Rawdon, H. S., *Discussion*, *ibid.*, 414.

Table 26.—Changes in "Alclad" Duralumin Due to Atmospheric Corrosion.

Location	Original Weight	Change in Weight, Grams			Tensile Properties after 6 yrs.		% Change in Tensile Properties		Remarks
		1 yr.	3 yrs.	6 yrs.	Tensile Strength	Elongation (%)	Tensile Strength	Elongation (%)	
Pittsburgh No. 1	167.76 171.26	+0.20 +0.18	+0.18 +0.14	+0.12 +0.11	58 845	17.1	−1.1 (*2.2*)*	−10.0 (*6.3*)*	Samples show some mechanical damage, surface generally dirty and roughened with very fine pattern of hard adherent scale.
Altoona No. 2	167.84 170.64	+0.18 +0.24	+0.14 +0.39	+0.11 +0.47	58 965	17.4	−0.9 (*2.0*)	−8.4 (*4.0*)	Samples show some mechanical damage, surface generally dark and dirty and roughened with very fine pattern of hard adherent scale.
New York City No. 4	169.40 173.25	+0.35 +0.32	+0.26 +0.24	+0.17 +0.16	59 255	18.9	−0.4 (*2.2*)	−0.5 (*3.5*)	Surface dirty and generally roughened with very fine pattern of hard adherent scale.
Rochester No. 6	169.77 169.48	+0.12 +0.11	+0.29 +0.22	+0.66 +0.38	58 245	15.6	−2.6 (*2.4*)	−17.9 (*19.7*)	Dull dirty film speckled with small spots of darker hard adherent scale.
Sandy Hook No. 5	171.53 173.09	+0.20 +0.23	+0.25 +0.26	+0.14 +0.16	58 945	18.3	−0.9 (*2.6*)	−3.7 (*3.5*)	Dull dirty film speckled with fine spots of darker hard adherent scale, dark scale along edges.
Key West No. 7	172.96 167.17	+0.09 +0.07	+0.14 +0.12	+0.20 +0.18	59 855	18.8	+0.6 (*2.4*)	−1.1 (*4.4*)	About 50 per cent of surface shows metallic luster; remainder, gray thin film with light scale spots resembling bird tracks, heavier scale near edges.
La Jolla No. 9	172.22 170.88	+0.62 +0.63	+0.55 +0.60	+1.13 +1.14	59 565	18.6	+0.2 (*2.0*)	−2.1 (*4.4*)	Dull gray thin scale with uniformly distributed mounds of heavier granular scale, 30 per cent of area still shows metallic luster.
State College No. 3	169.45 171.61	−0.01 +0.09	−0.03 +0.07	−0.05 +0.05	59 500	17.9	+0.1 (*2.5*)	−5.8 (*6.2*)	Generally discolored but still showing metallic luster, uniformly distributed small light gray spots over the mottled tarnished background.
Phoenix No. 8	170.06 168.98	+0.03 +0.03	+0.01 +0.01	+0.03 +0.03	59 080	19.3	−0.7 (*2.7*)	+1.6 (*3.5*)	Metallic luster generally visible over entire surface with a mottled pattern of gray spots, fine black spots uniformly distributed on numbered side.

* Italic figures in parentheses indicate maximum percentage difference due to chance.

action, that is, to provide for the development of an effective surface film, before widespread perforation of the coating occurs.[84]

One of the most extensive tests of the corrodibility of "Alclad" coatings in the atmosphere is that being conducted by the American Society for Testing Materials[85] at nine locations, which embrace a wide range of atmospheres. The results of this test at the end of six years for "Alclad-17ST" (Duralumin) 0.032 inch in thickness are given in Table 26. The pure aluminum layer on this stock is approximately 0.00176 inch in thickness.

It will be observed that after six years the alteration in physical properties is insignificantly small. The percentage change in tensile properties in almost all cases is shown to be less than the maximum change due to chance (italic figures in parentheses). The weight-increments over the period also are small and of the same order as those observed on commercial aluminum exposed in the same test. In contrast to these findings bare Duralumin also included in this test showed pronounced loss in tensile properties except in the two rural stations, State College, Pa., and Phoenix, Arizona. From these results it is clear that the aluminum coatings in this test are still intact and are providing adequate protection to Duralumin at the end of six years.

The resistance of calorized coatings to sulfurous atmospheres has been mentioned previously. Pure aluminum surfaces, similarly, resist corrosion satisfactorily in industrial atmospheres. Aluminum wire has been found superior in performance to copper wire in sulfur dioxide atmospheres prevailing in the neighborhood of smelters which treat sulfur-bearing ores. Seaside atmospheres on the other hand are relatively more active in stimulating corrosion of aluminum, owing to the tendency of chlorides to break down, penetrate or otherwise displace protective oxide films. "Alclad" Duralumin 0.064 inch in thickness has however shown satisfactory resistance to 20-per cent sodium chloride spray for periods up to eight years. This heavy-gauge "Alclad" sheet is employed for airplanes which are subjected to salt spray at intervals, but sea planes which experience more severe exposures are commonly constructed of painted "Alclad" sheet.[84] Studies have shown that the most effective painting procedure for marine use is a priming coat of zinc chromate in a synthetic resin vehicle, followed by two or three coats of aluminum paint in the same vehicle.[86] Paint coatings of this type are effective in preventing the corrosion of bare Duralumin and other aluminum alloys, particularly if the alloy surface is first anodically oxidized to provide a good bond for the paint coating.

Aluminum is resistant to distilled water and to ordinary fresh waters whether soft or hard. The presence of heavy metals, particularly copper, tin, lead and nickel, is deleterious, and waters which are high in chlorides or alkaline carbonates are corrosive. Most fresh waters contain silicates,

[84] Dix., E. H., and Mears, R. B., *Mech. Eng. (Am. Soc. Mech. Eng.)* 58, 784 (1936).

[85] Finkeldey, W. H., *Proc. Am. Soc. Testing Materials,* 38 (1938).

[86] Edwards, J. D., and Wray, R. I., *Ind. Eng. Chem.,* 27, 1145 (1935).

and as in the case of lead, silicate is a protective agent for aluminum in mildly alkaline solutions.

Numerous investigations have been made of the behavior of aluminum and aluminum coatings, as represented by "Alclad" products and sprayed aluminum, in seawater and salt solutions. It is perhaps sufficient merely to reiterate that aluminum is attacked by halogen salts but not by sulfates and nitrates.[87]

Aluminum coatings of the sprayed, dipped or "Alclad" type are probably unsuitable for protection of underground structures. Soil tests made a few years ago on specimens of sheet aluminum showed that the metal is badly pitted by contact with soil particles—the result, very likely, of differential aeration attack. Calorized coatings on steel pipe included in the Bureau of Standards soil test[54] were pitted at a lower rate than were bare steel specimens buried in the same test. It was found in this test, in which specimens calorized by both the powder and dipping processes were compared, that, while the powder-calorized coating was more effective in reducing pitting, it allowed a greater loss of weight than did the dip-calorized coating.

MISCELLANEOUS METALLIC COATINGS

Brass Coatings

The simultaneous electrodeposition of copper and zinc to form a coating of brass can be accomplished readily by the use of a cyanide solution of the two metals. In ordinary solutions, for example, sulfates, the difference of potential between copper and its solution (copper ions) varies so greatly from that between zinc and its solution (zinc ions), that the simultaneous deposition of the two metals is impossible. In a cyanide solution of the proper concentration, however, the potentials of the two metals are so nearly the same that copper ions and zinc ions can be discharged at the same time on the cathode, and a layer of brass is thus formed. Examination of the deposit formed by means of the x-ray diffraction method has shown that such a deposit is a true alloy of the two metals and not merely a mechanical mixture of small crystals of copper and zinc.

The essential constituents of a brass plating bath are copper and zinc cyanide and sodium cyanide. Sodium carbonate is sometimes added. The most suitable pH range appears to be 10.7 to 11.0. Cast brass anodes containing 70-80 per cent copper are generally employed and the bath is operated at about 32 to 45° C. (90 to 113° F.) at current densities from 0.2 to 1 ampere per sq. dm. (2 to 10 amperes per sq. ft.). Arsenic trioxide, phenol and ammonia in small quantities are sometimes employed as brightening agents to improve the appearance of the deposit. Steel strip is now coated with brass by annealing a duplex electrodeposit of copper and zinc for 10 to 30 minutes at a temperature between 700 and 1500° F.[87a]

---

[87] For a more extended review of the corrosion of aluminum in various media, see reference 84.

[87a] Thomas, C. G. (Thomas Steel Co., Warren, O.), *Private Communication*, October 27, 1938; Rubin, U. S. Patent 2,115,749 (1938).

Brass coatings are used quite extensively on iron and steel articles, especially upon builders' hardware, to give the appearance of solid brass. Such coatings are primarily for appearance. As a rule, they are very thin and afford little protection from atmospheric corrosive agencies. Brass-plated iron and steel articles rust very readily (even when lacquered) when used for out-of-door exposure, because such coatings are usually for decorative purposes and are very thin.

It is claimed [88] that brass is superior to copper as an intermediary layer or undercoating for nickel and chromium, owing to a greater tendency of these metals to adhere to brass. So far as is known, however, brass plating is not commonly employed for this purpose.

Brass plating has come into rather wide use lately to secure satisfactory adhesion of rubber coatings to metal. An important application is in connection with the attachment of rubber tires to steel tire rims where brass plating of the rims has proved to be the most feasible method of obtaining the necessary degree of adhesion of vulcanized rubber to the rim. In contrast to ornamental brass plating, where close control of color is desirable, brass deposited for rubber adhesion requires close control of composition. It has been found [89] that the most suitable range of composition is from 24.4 to 33.6 per cent zinc for the process employed. Deposits of about 0.00002 inch in thickness are generally employed. As would be expected, tarnish films usually reduce adherence. Brass appears to offer no advantage in the adhesion of Neoprene and rubbers vulcanized without sulfur.

Cobalt Coatings

Cobalt was electrodeposited as early as 1842, and it has long been known that the metal could be deposited readily on iron and other common metals. Cobalt ammonium sulfate or cobalt sulfate with sodium chloride may be employed as plating salts. The fact that a cobalt bath could be operated satisfactorily at current densities as high as 16.2 amperes per sq. dm. (150 amperes per sq. ft.)[90] stimulated considerable interest in cobalt plating a few years ago. Although the price of cobalt has been markedly reduced since the beginning of the present century, owing to the discovery of large cobalt ore bodies, the metal is still too expensive to permit commercial exploitation of cobalt coatings. As mentioned in Chapter 9, one of the processes for bright nickel coatings employs anodes containing 18 per cent cobalt and yields a bright deposit which is a cobalt-nickel alloy. Studies have been made of means of increasing the brightness of cobalt deposits.[91] Alloys of cobalt with nickel, and ternary alloys of cobalt, nickel and iron may be readily electrodeposited. Cobalt coatings are bluish-white in color, are somewhat similar to iron and nickel in hardness, and resemble nickel in their microstructure. There has been some controversy concerning the relative corrosion resistance of cobalt and nickel coatings. Although cobalt oxidizes somewhat more readily and is less resistant to weak acids than is nickel, its resistance to atmospheric corrosion appears to be of the same general order as that of nickel.

---

[88] Braun, A., *Oberflachentech.*, 12, 39, (Feb., 1935).

[89] Coats, H. P., *Monthly Rev. Am. Electroplaters' Soc.*, 24, 5 (1936).

[90] Kalmus, H. T., Harper, C. H., and Savell, W. L., *Trans. Am. Electrochem. Soc.*, 27, 75 (1915).

[91] Chaybany, A., *Met. Ind. (London)*, 48, 721 (1936).

Tungsten Coatings

Tungsten was first electrodeposited from fused salt baths. For example, smooth, but thin, deposits were obtained from sodium and lithium tungstates containing tungstic acid at temperatures above 1000° C. (1832° F.), operating at 70 to 80 amperes per sq. dm.[92] These deposits, however, have not been of any commercial importance. More recently tungsten has been successfully deposited from aqueous solutions, notably from an alkaline sodium tungstate solution.[93] The bath, consisting of tungstic acid dissolved in sodium carbonate and having a pH value of 12 to 13, is most suitably operated at about 95° C. at current densities from 8 to 10 amperes per sq. dm. (75 to 100 amperes per sq. ft.). The tungsten coating obtained in this process is smooth, hard, highly lustrous and of a bluish-white color. It is, however, very thin, the deposition process apparently ceasing after the deposition of from 0.003 to 0.05 gram of tungsten per square decimeter of surface area. The plating bath after a period of usage appeared to become exhausted and failed to deposit tungsten. Subsequently it was shown[94] that the addition of very small proportions of iron to a tungsten bath, which had been depleted in this manner, tended to restore or regenerate it; and furthermore it was found that deposits could not be obtained from baths made from highly purified salts. This experience and the fact that iron was invariably found in tungsten deposits from ordinary alkaline carbonate, and also phosphate and citric acid baths, led to the conclusion that iron is present in tungsten deposits from aqueous tungsten plating baths.

As would be expected from the foregoing discussion, alloys of tungsten with iron and also with nickel, cobalt, tin and a variety of other elements may be electrodeposited.[95] Coatings of alloys of tungsten with 65 per cent of nickel or tantalum may be plated in various thicknesses. These deposits have a high luster and are similar in porosity to nickel coatings of the same range of thicknesses.

Pore-free coatings of the nickel and tantalum alloys of tungsten show excellent resistance to attack by strong acids, alkalies and salt solutions. As yet, however, these coatings have not attained any appreciable commercial use. Coatings of tungsten, as well as of molybdenum and tantalum, can be produced by cementation on iron and copper alloys. This is readily accomplished by embedding the metal to be coated in the appropriate ferro-alloy at 800 to 1200° C. (1650-2200° F.) in the presence of ammonium chloride vapor.[96] It has been shown also that coatings of boron, tantalum, vanadium, cobalt, uranium, silicon, zirconium, and titanium can be produced on steel by cementation methods.[97] As in the case of chromizing and calorizing, which have been described previously, coatings of the metals mentioned above do not consist of the pure metal, but of a combination of the coating and the basis metal. Although the composition and properties of these coatings have not been studied extensively, it is reported that cemented molybdenum and tungsten coatings are acid-resistant and that zirconium coatings are resistant to oxidation at high temperatures.

---

[92] Van Liempt, J. A. M., *Z. anorgan. Chem.*, **122**, 175 (1922); 143, 285 (1925).

[93] Fink, C. G., and Jones, F. L., *Trans. Electrochem. Soc.*, **59**, 461 (1931). Fink, C. G., U. S. Patent 1,885,702, (Nov. 1, 1932).

[94] Holt, M. L., *Trans. Electrochem. Soc.*, **66**, 453 (1934).

[95] Holt, M. L., *Trans. Electrochem. Soc.*, **71**, 301 (1937).

Tantalum Coatings

Tantalum occurs in nature together with the element columbium in a mineral known either as tantalite or columbite, depending upon which of the two predominates in concentration. Both minerals are tantalates and columbates of iron and manganese. Tantalite is obtained from Western Australia and from the Black Hills district of South Dakota, and it occurs in concentrations so low that approximately two and one-half tons of rock are required to produce one pound of tantalum.[98]

The ore is treated chemically to produce tantalum salts from which the metal is obtained in the form of powder by reduction. The methods of powder metallurgy (high pressure and sintering, in this case, in a vacuum) are employed to produce bars from which ductile and malleable sheets of the metal may be obtained.

Tantalum coatings may be applied by metal spraying. Inasmuch as thickness of deposit of from 0.070 to 0.100 inch is required to overcome porosity, the use of sprayed tantalum has been restricted to certain special applications, such as to the shafts of pumps to be used for acids. It is more common in the manufacture of corrosion-resisting equipment to employ what is known as sheet-metal technique. In this process, thin sheets of tantalum are welded to the surfaces of steel and certain other metals. Such coatings are, of course, continuous in character.

Tantalum coatings have come to be used in recent years in chemical equipment employed in the processing of chlorine compounds, and strong acids. Hydrofluoric acid, fluorides, and hot or fuming sulfuric acids attack the metal. At approximately 175° C. tantalum reacts with chlorine.

---

[96] Laissus, J., *Compt. rend.*, 182, 1152 (1926).

[97] Laissus, J., *Chim. Ind.*, 29, 515 (1933).

[98] The authors are indebted to the Fansteel Metallurgical Corporation of North Chicago, Illinois, for much of the information given concerning tantalum coatings.

Chapter 11

Coatings of Noble and Rare Metals

HISTORY OF GILDING AND SILVERING OF METALS

Historically, the first metal coatings were those of gold and silver. Although the idea of ornamentation was always foremost in the minds of the users of such coatings and still remains so, they are, nevertheless, properly to be considered as protective coatings. At the present time gold and silver coatings are used in some instances, although to a very limited extent, primarily as a protection against severe corrosive attack; typical examples are the silver lining of autoclaves, the gold plating of the interior of bomb calorimeters and the gold plating of standard weights and other laboratory equipment. The silver plating of the fixtures used for dispensing soda water and similar drinks is an example of the use of silver plating on a larger scale.[1] Lately the use of silver-lined equipment in the food industry has been extended. Coatings of silver, gold, platinum and palladium are coming to be used for electrical contacts.

The gilding and silvering of metals has been practiced for centuries and many ingenious methods have been developed. The earliest method depended upon the use of gold hammered into foil. This practice was known in Egypt as early as 3000 B. C. Gilding and bronzing by means of finely powdered metal in suspension in a suitable vehicle followed. Fire or amalgam-gilding, which was applicable to silver as well as to gold, was known, at least in a crude form, as early as 300 A. D.[1a] In this method the surface to be coated, usually brass or copper, was first treated with a solution of mercurous nitrate and then rubbed with an alloy consisting of 9 parts of mercury to 1 part of gold. After the surface had been thoroughly amalgamated, the mercury was expelled by means of heat. This could be repeated more than once if a very heavy coating was desired. The use of the mercury insured intimate alloying between coating and base. It is claimed by some that such coatings are much superior to the modern electroplated gold coatings, and the process is still used to a very limited extent.

The method of "close plating"[2] was formerly widely used for producing silver-coated articles and was the immediate predecessor of the fusion method which we know principally as the method for making "Old Sheffield Plate."

---

[1] The American Silver Producers Association has in progress an extensive research program directed toward the development of wider industrial use of silver and silver coatings. For a discussion of the properties and industrial uses of silver see: Rogers, B. A., Schoonover, I. C., and Jordan, L., *Nat. Bur. Standard Cir.*, C 412 (1936); Lee, J. A., *Ind. Eng. Chem.*, **28**, 1412 (1936).

[1a] Theobald, W., *Ding. Poly. J.*, **328**, 163 (1913).

[2] Bradbury, F., "History of Old Sheffield Plate," London, MacMillan & Co., 1912.

In close plating, the finished article was cleaned with ammonium chloride and then dipped into molten tin. A thin foil of silver cut to the approximate size and shape needed was carefully fitted over the article and a hot soldering iron lightly rubbed over it. The tin melted and soldered the silver coating in place, after which the article was burnished and polished. Close plating was applied to articles of rather complex shape including knives, forks and spoons and other tableware, as well as buttons, buckles, snuff boxes, spurs and other articles for personal adornment. Close-plated articles could not be heated; otherwise the tin solder would melt and the coating would strip off. Neither would it withstand very severe corrosive conditions, because blisters formed as a result of corrosive attack beneath the coating. The method is still in use today, however, in a few special cases.

The fusion method of silver plating copper was discovered by Thomas Boulsover about 1743. In brief, this consisted in heating a slab of copper, with a thinner plate of silver in close contact, nearly to the fusion temperature of silver, and subsequent rolling of the composite slab into sheet form. First of all, the slab, which, though described as copper, was an alloy of copper with some zinc and lead, was planed off to a very smooth surface as was likewise the silver plate, the thickness of which depended on the final thickness of silver plating desired. For double-coated sheet both sides of the copper slab were treated. The copper slab and silver plates were pressed firmly together, covered with sheet copper which had previously been dressed with powdered chalk to prevent it from fusing to the silver, bound with iron wire and heated until the silver began to "weep." It was then removed from the furnace, stripped of its copper sheathing, cleaned and rolled into sheet form. From this composite sheet many intricate and complex shapes were worked out, which are known to us as "Old Sheffield Plate." With the discovery and commercial development of the cheaper electrolytic method of silver plating, the fusion method passed out of use.

ELECTROPLATED SILVER COATINGS

The commercial application of the electrodeposition of silver dates from about 1840 with the discovery by John Wright, a young surgeon of Birmingham, England, that a cyanide solution of silver must be used in order to obtain a dense, uniform adherent coating of silver. Cyanide solutions are still used today almost exclusively in the silver-plating industry. These solutions possess many advantages, such as high anode and cathode efficiencies and good plating characteristics over a wide range of solution composition, temperature and current density. The silver cyanide bath is prepared by dissolving silver cyanide in potassium or sodium cyanide, forming thereby a double cyanide. In recent years the sodium salt has come to be largely used for this purpose although the potassium compound is preferable, as it possesses a high conductivity and a wider plating range in terms of current density.[3] The plate from the potassium solution is said to be superior in physical appearance and may be burnished more satisfactorily than that from sodium cyanide.[4] Owing to the poisonous nature of cyanide solutions, many attempts have been made to deposit silver from solutions of other silver salts such as the sulfate, nitrate, fluoride and fluoborate,[5] but the results have been unpromising. Recently, however,[5a] deposits have been obtained from acid complex iodide baths which are said to be equivalent in quality to those obtainable from cyanide baths.

---

[3] Egeberg, B., and Promisel, N., *Trans. Electrochem. Soc.*, 59, 287 (1931).

Silver deposits from cyanide solutions have a milky or frosted appearance and may require buffing to secure a bright surface. To overcome this difficulty it has long been customary to add to the plating bath small proportions of carbon disulfide as a brightening agent. More recently it has been shown that the addition of about 1 gram of sodium thiosulfate and 10 cc. of ammonia per liter of plating solution is more effective than is carbon disulfide in producing a bright white silver deposit.[6]

Numerous variations may be necessary in the preliminary treatment of metals to be plated, such as "strikes" and "dips" in various solutions before immersion in the plating bath. Most metals tend to precipitate silver from solution by simple immersion, and this tendency is minimized by "striking" the basis metal at high current densities in solutions of low metallic ion concentrations—usually dilute cyanide solutions. Another method of reducing immersion plating and securing deposits of improved adherence is to flash the metal to be plated with a thin layer of a metallic deposit which shows a lesser tendency to replace silver from solution. There appears to be some advantage in a preliminary copper strike followed by a silver strike in the silver plating of steel surfaces. By this means adherent smooth deposits 0.05 to 0.07 in. in thickness may be obtained.[6a]

Thickness of Silver Plating

It was formerly the custom in describing silver-plated ware to use such designations as "triple-plated," "quadruple-plated," and the like. The use of these misleading terms has now been discontinued by American manufacturers and the weight of silver, for example, per unit of surface area as on a stated number of articles of similar kind and size, is used instead to indicate the thickness of the coating. Table 27 gives the average thickness of the coating on silver-plated tableware as adopted under the NRA and since generally accepted.[7] The Federal Specification Board specifies for all pieces an average thickness of silver of 0.00125 in. This corresponds to 1 troy ounce per square foot. For overlay 0.0018 in. is specified.[7a]

---

[4] Mesle, F. C., *Monthly Rev. Am. Electroplaters Soc.*, **15**, No. 10, p. 4 (1928).

[5] Sanigar, E. B., *Trans. Electrochem. Soc.*, **59**, 307 (1931).

[5a] Alpern, D. K., and Toporek, S., *Trans. Electrochem. Soc., Preprint* **74**, No. 14 (1938).

[6] Pan, L. C., *Trans. Electrochem. Soc.*, **59**, 329 (1931).

[6a] Mathers, F. C., and Gilbertson, L. I., *Trans. Electrochem. Soc., Preprint* **74**, No. 30 (1938).

[7] *Metal Ind. (New York)*, **32**, 340 (1934).

[7a] Federal Specification Board Specification RR-T-51a, June 5, 1934.

Table 27.—Average Weight of Coating on Silver-Plated Tableware.

	Teaspoon (Oz. Silver Per Gross)	Dessert Spoon Dessert Fork R.B. Soup Spoon (Oz. Silver Per Gross)	Tablespoon Dinner Fork (Oz. Silver Per Gross)
"A1" or "Standard"	2	3	4
"AA"	3	4½	6
"Double" or "X"	4	6	8
"Triple" or "XXX"	6	9	12
"Quadruple" or "XXXX"	8	12	16

It is also necessary to take into account the thickness of the coating on those portions of plated tableware which are subjected to the greatest wear, such as the back of the bowl of spoons or the tines of forks. It is common practice, for the better grade of tableware, to use a heavier coating on such portions. This is obtained either by use of a silver insert in the "blank," which is later plated, or by a supplementary plating of the desired portions after the article has been given the regular plating. The specification referred to above requires the silver coating to be 0.0012 inch thick on such spots.

Defects in Silver Coatings

The occurrence of red stains on silver-plated articles is sometimes the cause of considerable concern to silver platers. This defect has been shown[8] to arise during the polishing operation; it appears to be related to improper use of the polishing rouge on a surface while still heated by the polishing operation.

"Spotting out" on silver-plated surfaces is another defect. These white spots, which do not appear until some time after the article has been removed from the plating bath, are to be ascribed primarily to inclusion of some of the cyanide in the coating. The exact nature of the defect, however, has not been fully established.

At times difficulty is experienced in polishing silver coatings. The coating in such cases often has a coarse crystalline appearance which is removed with difficulty by ordinary polishing methods. It has been reported that silver may be electrodeposited under certain conditions so that the crystals of the silver form as extensions of the pre-existing crystals of the nickel-silver base metal (compare Figure 46). Such coarsely grained silver coatings cannot be satisfactorily polished by the methods usually employed. It has not been established, however, that this is the only cause for irregularities in the polishing of silver-plated coatings.

Tarnishing of Silver

Silver readily tarnishes upon exposure to industrial atmospheres or indoor air contaminated by the products of combustion of sulfur-bearing fuels. Foods such as onions and eggs, which contain organic sulfur compounds, are also well known to tarnish silver.

---

[8] Jefferson, A., *J. Inst. Metals*, 28, 447 (1922).

The tarnish film which forms on silver exposed to the air is composed of silver sulfide and contains no oxide. Even when silver which has been previously oxidized is exposed to the air the film becomes converted into sulfide. The gain in weight of silver with time of exposure to the atmosphere is parabolic in type. This suggests that the process is controlled by diffusion. It has been proposed recently that the tarnishing process is electrolytic in character [8a] and that the rate of tarnishing of silver is probably controlled by the mobility of silver ions, which is unusually high.[8b] The rate of tarnish does not appear to be appreciably influenced by the variation in humidity prevailing indoors throughout the year. Unlike the behavior of many of the base metals, there does not appear to be in the case of silver a critical relative humidity above which the rate of corrosion is abruptly and markedly accelerated.

In appearance tarnish films on silver exhibit the usual range of interference colors. There seems to be little relationship between the appearance of tarnished silver and its electrical contact resistance.

The removal of the tarnish film on silverware may be accomplished by polishing the surface with a fine abrasive or by electrolysis. If, in a solution of sodium chloride and sodium carbonate, both of which are common household materials, a tarnished silver article is placed in contact with a metal, such as zinc or aluminum, it will be detarnished. The base metal serves as anode, the silver as cathode, and by means of cathodic action the silver sulfide is reduced to silver. Silver knives with stainless steel blades should not be subjected to this treatment. There is no appreciable loss of silver in the reduction process. If the silver has been very severely tarnished, the surface after cleaning is dull on account of the thin film of "moss" silver formed by reduction of the sulfide. Buffing may be necessary in such cases to restore the polish.

Attempts have been made to improve the tarnish resistance of silver by the codeposition of another metal. Silver-cadmium alloys were proposed for this purpose [9] but it was found that alloys containing 3 per cent or more of cadmium possess an undesirable yellowish tinge.[10] An electrodeposited silver-cadmium alloy containing about 24 per cent of silver has been recommended for its light-reflecting properties inasmuch as it maintains its reflecting power to a greater degree than does silver when both are tarnished.[11] Alloys of silver with indium may be plated and are claimed to possess superior resistance to tarnish.[12] Silver-lead alloys are said to tarnish more readily than silver alone.[12a] A recent extensive study of the tarnishing of silver and silver alloys[8b] indicates that the most feasible method of preventing tarnish is to provide a surface film of high electrical resistance. This is most successfully accomplished either by the selective oxidation of aluminum or beryllium in silver alloys or by the superimposition of cathodically deposited films of these oxides on pure silver or its alloys.

[8a] Wagner, C., *Z. phy. chem.*, **B 21**, 25 (1933); **32**, 447 (1936); Hoar, T. P., and Price, L. E., *Trans. Faraday Soc.*, **34**, 867 (1938).

[8b] Price, L. E., and Thomas, G. J., *J. Inst. Metals*, **63**, (1938), (Advance copy).

[9] Proctor, C. H., *Metal Ind. (New York)*, **18**, 13 (1920).

[10] Aten, A. H. W., and van Putten, M. F., *Rec. trav. chim. des Pays-Bas*, **44**, 861 (1925).

[11] Stout, L. E., and Thummel, W. G., *Trans. Electrochem. Soc.*, **59**, 337 (1931).

[12] French Patent 699,068 (1930); Gray, D., Bailey, R. O., and Murray, W. S., U. S. Patent 1,847,941 (1932).

GOLD COATINGS

Gold coatings are applied by electroplating and by gold-filling—a process which resembles that employed in making Old Sheffield plate. Because of the highly electropositive or noble character of gold, coatings of this metal do not afford any electrochemical protection to base metals. The resistance of gold to chemical attack and tarnish makes it a particularly desirable metal to use in highly corrosive environments provided the coating is substantially pore-free. Gold coatings are widely used for certain types of electrical contacts, notably on the electrodes of telephone transmitters.

Gold electroplating solutions usually consist essentially of the double cyanide of gold and potassium. Sodium cyanide may be employed in place of the potassium salt and in some cases a small percentage of sodium phosphate is added to the solution. Gold baths are operated in the temperature range 45 to 80° C. (113 to 176° F.) and at current densities from 0.1 to 0.5 ampere per sq. dm. (1.0 to 5.0 amperes per sq. ft.). By varying the composition of the plating solution, that is, by adding other metals such as silver, copper and nickel, coatings of green, red and white colors may be obtained. These deposits are in reality alloys of gold and the other metal.

Gold can also be plated without the application of an electromotive force external to the plating cell. One such method merely requires setting up a primary battery which uses two solutions; one of them, the gold solution, is kept separate from the second one, sodium chloride, by means of a porous cup. A strip of zinc, the anode of the cell, is immersed in the sodium chloride solution; the article to be plated, either brass or copper, is hung in the gold solution within the porous cup. Electrical contact by means of a wire is made between the two electrodes, that is, the zinc strip and article to be plated. In such a cell, gold from the solution deposits upon the surface of the cathode (article to be plated) when a current is allowed to flow by connecting the anode and cathode by a wire. The deposit is very uniform and adherent. A much simpler method merely requires immersion of the article, brass or copper, in a gold solution of the proper composition. In this case, the article is plated by the passage of a slight amount of copper or zinc into solution and the precipitation of an equivalent amount of gold on the surface. The coating obtained is very adherent but exceedingly thin and the method is used only for small, cheap articles. Such coatings are only a few millionths of an inch in thickness.[13]

[12a] Mathers, F. C., and Johnson, A. D., *Trans. Electrochem. Soc., Preprint* 74, No. 27 (1938).

Electroplated gold coatings are fine-grained and dense in structure. It is possible to deposit gold coatings on brass in thicknesses of the order of 0.0001 inch which show no evidence of pinhole corrosion in the usual accelerated corrosion tests. Generally for contact surfaces, deposits of 0.0005 inch are recommended.[14] The use of nickel as an undercoating for gold has been recommended for the protection of steel.[15]

"Gold filled" articles, such as watch cases, are stamped from gold-plated sheet made by soldering a sheet of gold or gold alloy to a slab of nickel-silver or brass. The soldering is accomplished by inserting a thin sheet of "brazing" alloy between the gold and the basis metal. It is necessary to heat the material only above the melting point of the braze which is considerably lower than that of either the gold or the basis metal.

According to a decision, January 25, 1923, of the U. S. Federal Trade Commission relating to the gold-filled watch-case industry, the minimum thickness of the gold layer on such gold-filled plate must be 0.003 inch on the outside of the case and 0.001 inch on the inside.

By the use of proper reducing solutions gold and silver can be reduced to the metallic form from their solutions, and coatings obtained directly by this means. This method is used principally for the production of mirrors, however, rather than for coating other metals.

Rhodium Coatings

Rhodium may be electrodeposited as a bright pinkish-white coating which is not tarnished appreciably in the air and which is not dissolved even in hot aqua regia.[16] It has come into commercial use in the jewelry and reflector industries where tarnish resistance and high reflectivity are attractive attributes. In the manufacture of reflectors for searchlights rhodium is deposited on undercoatings of electrodeposited copper.[17] There is some doubt as to the suitability of rhodium coatings for the protection of silver tableware from tarnish. For one thing rhodium differs slightly from silver in appearance. While rhodium is somewhat harder than silver, it may be expected to be scratched and otherwise damaged by the usage to which tableware is subjected, with the result that the rhodium coating will be removed in places, permitting the underlying silver to tarnish and darken. It is reported that rhodium-plated silver contacts have been used successfully in telephone apparatus.[18]

Rhodium may be plated from a sulfate bath containing ammonium sulfate operating at about 50° C. (122° F.) and at current densities not to exceed 9 amperes per sq. dm. (0.6 ampere per sq. in.).[19] Very satisfactory deposits may be obtained also from a solution of ammonium rhodinitrite.[16]

---

[13] Blum, W., and Hogaboom, G. B., "Principles of Electroplating and Electroforming," 2nd ed., New York, McGraw-Hill Book Co., 1930.

[14] Anon., *Oberflächentechnik,* **14,** 2 (1937).

[15] Leonhardt, R., and Steel, P., *Oberflächentechnik,* **10,** 83 (1933).

[16] Atkinson, R. H., and Raper, A. R., *Metal Ind. (London),* **44,** 191 (1934).

[17] Schwartz, M. W., *Metal Ind. (New York),* **36,** 14 (1938).

[18] Anon., *Funktech. Monat.,* No. 2, 68 (Feb., 1936).

Rhodium coatings are generally of the order of 0.00001 inch in thickness. Attempts to produce appreciably heavier coatings have not been successful.

PLATINUM AND PALLADIUM COATINGS

Platinum and palladium coatings have been used, like gold, to a limited extent for protective coatings and for electrical contacts. Platinum has been electroplated for many years, usually from a complex phosphate bath. More recently it has been shown that both platinum and palladium may be more satisfactorily deposited from amminonitrite solutions.[20] These baths are used at 90-95° C. (194-203° F.). The throwing power of the solutions is good enough to permit satisfactory covering of all recessed areas of jewelry parts. The coatings are bright and do not require buffing. A non-porous deposit of palladium requires a coating 0.0002 inch in thickness.[21] Coatings of the platinum metals, notably palladium, may be fabricated by mechanical methods. This may be accomplished by welding layers of the noble metal on nickel strip and rolling down to the desired dimensions.

INDIUM COATINGS

Indium is one of the rarer elements. It usually occurs in small amounts with certain zinc ores from which it is recovered by chemical and electrochemical methods.[22] Indium is a very soft, ductile metal of a gray, lustrous appearance. It melts at 115° C. The metal is now available in commercial quantities.[23]

Although indium was electrodeposited as long ago as 1904, it was only recently that a practical plating process was developed.[24] The plating bath is prepared by dissolving precipitated indium hydroxide in a concentrated sodium cyanide solution and adding 0.5 gram of glucose for each gram of indium present.[25] The bath is operated at room temperature at current densities from 1 to 16 amperes per square decimeter.

Indium electrodeposits are silver-white in color and of a satin-like texture. Indium remains bright in the air and is more resistant to tarnish than is silver. The coating is soft and may be scratched with the fingernail. As mentioned previously in the discussion of tarnish-resistant silver alloys, it is possible to electrodeposit alloys of indium with silver. These alloys are harder than either of the two metals alone.

---

[19] Fink, C. G., and Lambros, G. C., *Trans. Electrochem. Soc.*, 63, 181 (1933).

[20] Keitel, W., and Zschiegner, H. E., *Trans. Electrochem. Soc.*, 59, 273 (1931).

[21] Atkinson, R. H., and Raper, A. R., *J. Electrodepositors' Tech. Soc. (London)*, 10, 1 (1933).

[22] Westbrook, L. R., *Trans. Am. Electrochem. Soc.*, 57, 289 (1930).

[23] Murray, W. S., *Ind. Eng. Chem.*, 24, 686 (1932).

[24] U. S. Patents 1,847,941 (March 1, 1932); 1,849,293 (March 15, 1932).

[25] Gray, D., *Trans. Electrochem. Soc.*, 65, 377 (1934).